Generating Phosphinidenes: New Approaches

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VRIJE UNIVERSITEIT

Generating Phosphinidenes: New Approaches

ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad Doctor aan
de Vrije Universiteit Amsterdam,
op gezag van de rector magnificus
prof.dr. T. Sminia,
in het openbaar te verdedigen
ten overstaan van de promotiecommissie
van de faculteit der Exacte Wetenschappen
op donderdag 1 december 2005 om 13.45 uur
in het auditorium van de universiteit,
De Boelelaan 1105

door
Marcus Leonardus Gerardus Borst
geboren te Heerhugowaard

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copromotoren:	dr. M. Schakel
	dr. A.W. Ehlers

now we know in part,
one day we shall know fully
even as we are fully known

1 corinthians 13,12

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Chapter 1

Generating Phosphinidenes: New Approaches
An Introduction

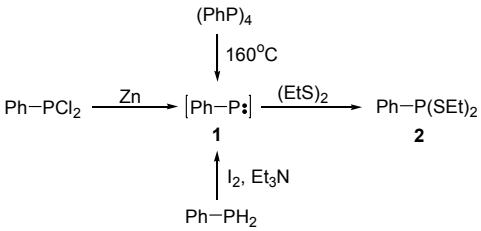
Reactive intermediates[1] are – by definition – short-living and therefore often hard to determine or identify. Still, reactive species have always attracted chemists, either from a synthetic, analytic, physical or theoretical point-of-view, not only owing to the challenges involved, but also because reactive intermediates have unusual, and therefore fascinating, electronic structures. In addition, due to their high reactivity they often provide access to complex and synthetically valuable molecules. In this thesis new approaches to one particular class of reactive intermediates, phosphinidenes, will be presented.

Phosphinidenes [R-P] are the phosphorus analogues of carbenes [R_2C] and nitrenes [R-N]; all three are neutral six-electron species. In contrast to the scarce reports on the determination of phosphinidenes, there are numerous examples where carbenes or nitrenes have been detected. Additionally, the generation of carbenes has become a standard laboratory procedure and is used to synthesize complicated molecules. Furthermore, since the early 1990s stable carbenes are known and these are extensively used as ligands in transition-metal complexes.[2] Illustratively, in a recently published comprehensive volume on reactive intermediates five chapters concern with carbenes, two are dealing with nitrenes and only four out of all 1072 pages are devoted to phosphinidenes.[1]

This chapter will introduce the reader to what is known about phosphinidenes, starting with free phosphinidenes, followed by a discussion of phosphinidenes complexed to transition-metals.

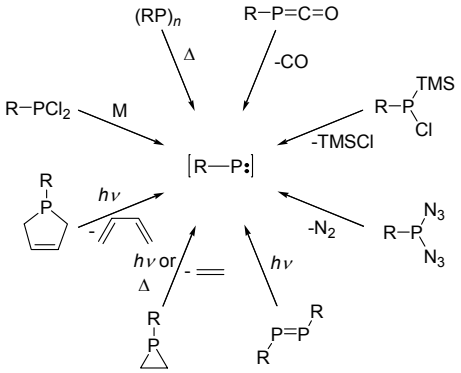
1.1 Free Phosphinidenes

Phosphinidenes are monovalent and neutral species, which may exist either in their singlet or triplet state. The triplet state is the ground-state for parent species [P-H] and a laser photoelectron spectrometry study determined the triplet-singlet gap to be 21.9 kcal/mol.[3] High-level computational studies agree on a triplet ground-state and reported a triplet-singlet splitting for alkyl- and aryl-phosphinidenes of a similar magnitude (22-23 kcal/mol).[4] Substitution of the phosphinidene with either $-PH_2$ or $-NH_2$ leads to a considerable stabilization of the singlet state. If one of the hydrogens is replaced with a methyl-group the singlet-state is calculated to be the ground-state, albeit by small amounts (-PHMe: –0.6 kcal/mol, -NHMe: –1.2 kcal/mol).[4b]



Scheme 1 – Proposed formation of phenylphosphinidene **1**.

The first claim of the intermediacy of a free phosphinidene in a reaction was made in 1965 by Schmidt who proposed the formation of phenylphosphinidene [Ph-P] **1** from either cyclopolyphosphines, dichloro phenylphosphine and zinc, or phenylphosphine and iodine, solely on the basis of the resulting dithioester **2** in all three reactions (see Scheme 1).[5-6] Subsequent attempts followed these approaches, exploiting the thermal depolymerization of cyclopolyphosphines or the reduction of dihalophosphines with a variety of metals.[7] Later, photolysis of diphosphenes was reported to yield an intermediate phosphinidene and[8] more recent approaches drew on the elimination of thermodynamically stable molecules like olefins,[9] nitrogen, carbon monoxide[10] or trimethylsilylchloride[11] from suitable precursors (Scheme 2).



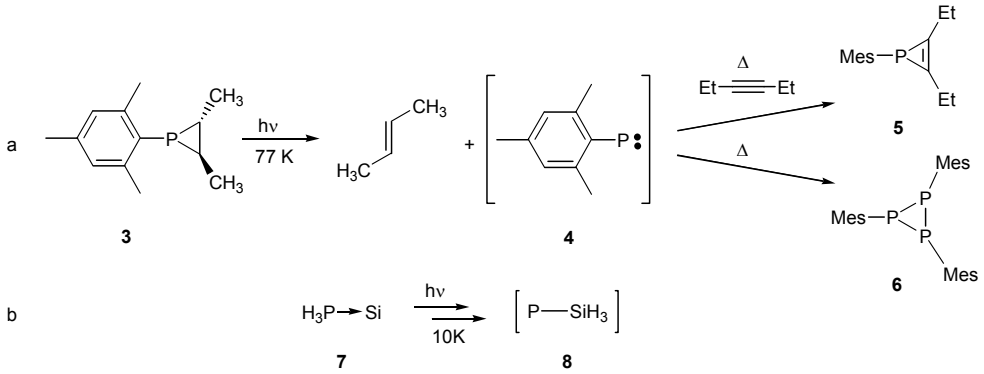
Scheme 2 – Generation of uncomplexed phosphinidenes.

The intermediacy of free phosphinidenes has not been established firmly in all cases and it has rightfully been stressed that the effective involvement of a phosphinidene in the reactions of any potential precursor cannot easily be demonstrated.[12] Evidence should not only be based on the final products, whose formation may be explained by a phosphinidene intermediate, but also on spectroscopic proof and/or thorough kinetic research of the reactions alleged to involve these intermediates. Additionally, calculations can be used to support or exclude the transient existence of phosphinidenes. For example, a recent computational paper showed a thermal formation of arylphosphinidene from phosphiranes to be highly unlikely.[13]

Spectroscopic Detection. In 1994 Gaspar and co-workers, in a break-through experiment, confirmed mesitylphosphinidene **4** (mesityl = 2,4,6-trimethylphenyl) to be a triplet species using electron paramagnetic resonance spectroscopy (EPR): for the first time direct spectroscopic evidence was found for a free phosphinidene.[14] When a frozen (77K) solution of phosphirane **3** in methylcyclohexane was irradiated with light at 254 nm an EPR signal could be obtained with an unusually large zero-field-splitting parameter D of $|D/hc| = 3.521$ cm^{-1} (Scheme 3a). This signal was attributed to [MesP] and the significant size of D to spin-orbit coupling. A more recent computational study confirmed this assumption and calculated a $|D/hc|$ of 3.46 cm^{-1} for triplet [Me-P].[4d]

Additional proof for the formation of [MesP] was given by the trapping of intermediate **4** with 3-hexyne to form 1-mesitylphosphirene **5** after thawing of a poisoned matrix. In the absence of a trapping reagent cyclopolyphosphine **6** was formed. No other spectroscopic data were reported. Yoshifuji and co-workers tried to repeat this experiment with larger phosphorus substituents but were unable to reproduce the EPR signal found by Gaspar and co-workers.[15]

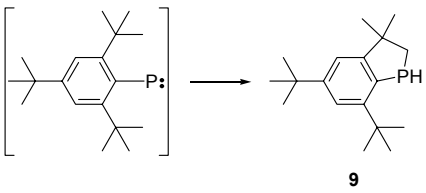
Recently, Glatthaar and Maier analyzed the photo-induced reactions of matrix-isolated[16] silicon-PH_3 adduct **7** at 10K and found that extensive irradiation of **7** ($\lambda = 366$ nm) resulted in the formation of triplet silylphosphinidene **8** (Scheme 3b).[17] No EPR spectroscopy was attempted, but the experimental IR spectrum, characterized by a strong absorption at 884.9 cm^{-1}, could be reproduced with a calculated spectrum of triplet **8**.[17]



Scheme 3 – Photochemical generation phosphinidenes.

Until very recently all experimental studies on parent phosphinidene [P-H] were gas-phase studies, but lately the first report on matrix-isolated [P-H] appeared.[18] Parent phosphinidene was trapped in an inert, solid matrix, after subjecting a mixture of PH_3 and a noble gas to a discharge and subsequent deposition on a cooled sapphire window ($T < 20$ K) yielded matrix-isolated [P-H]. Consecutively, the magnetic circular dichroism of one of the absorption bands was studied.

The reactivity of free phosphinidenes is so far of limited synthetic use. Insertion of phosphinidenes into O-H and S-S bonds has frequently been observed, as well as the addition to conjugated dienes.[7] The addition to non-conjugated carbon-carbon unsaturated bonds has only been reported for phosphino-phosphinidenes[19] and in the photolytic decomposition of phosphiranes.[9] A characteristic reaction of phosphinidenes bearing a supermesityl ligand (2,4,6-tri(*t*-butyl)phenyl, Mes*) is the insertion into a C-H bond of one of the *tert*-butyl groups resulting in phosphaindane **9** (Scheme 4).[8-9]



Scheme 4 – C-H insertion of [Mes*P].

1.2 Terminal Phosphinidene Complexes [R-P=ML$_n$]

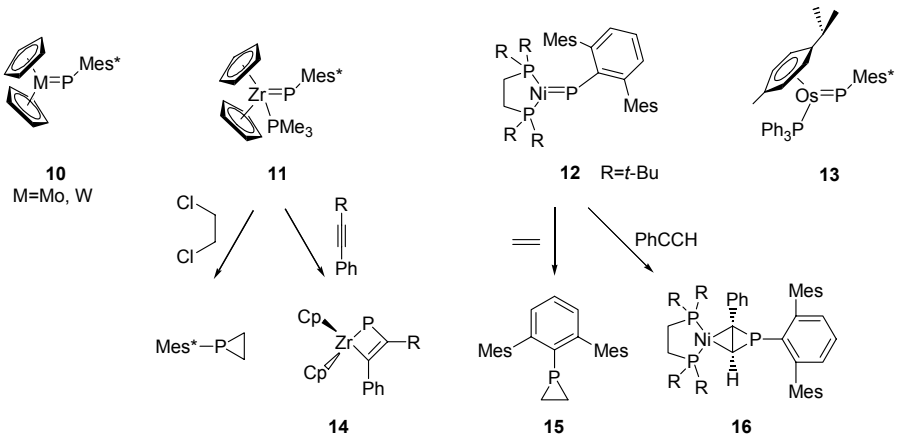
Phosphinidenes can be complexed to transition-metals and several bonding-modes are possible, but for a synthetic purpose terminally coordinated phosphinidene complexes are most interesting. The low degree of coordination of the phosphorus atom enhances the reactivity of terminal phosphinidene complexes with respect to phosphinidenes in other bonding modes.

Transition-metal complexation as such has two notable effects on the phosphinidene. The first effect is a partial occupation of the unoccupied phosphorus p_{π^*} acceptor orbital through metal-ligand back-bonding and a consequent preference of the singlet over the triplet state.[20] For example, for $W(CO)_5$-PH the singlet state was calculated to be 9.3 kcal/mol more stable than the triplet state and substitution with amino- or hydroxy-groups increased the singlet-triplet gap even more (> 22 kcal/mol).

A second effect has its origin in the ligands at the metal, which determine the philicity of the phosphorus atom: electron-withdrawing ligands with strong π-acceptor capabilities reduce the charge concentration on the phosphorus atom and enhance the electrophilicity of the phosphinidene complex. Ligands with strong σ-donor capabilities increase the electron density on the phosphorus atom and increase its nucleophilicity.[21] It is striking that all stable phosphinidene complexes isolated so far have been of the nucleophilic type, with the exception of a handful positively charged electrophilic phosphinidene complexes. The two classes of phosphinidenes will be discussed shortly, with an emphasis on the electrophilic ones because these will be the focus of this thesis.

1.2.1 Nucleophilic Phosphinidene Complexes

In 1987 Lappert and co-workers[22] reported the first stable Mo- and W-complexed phosphinidenes **10** and since then many more have been synthesized, with a variety of metals (Ti[23], Zr[24], V[25], Nb[26], Ta[27], W[28], Ru, Os[29], Co, Ru, Ir[30] and Ni[31]) and one thing in common: at least one π-donating ligand at the metal-fragment. Typical examples are shown in scheme 5. On the basis of the orientation of the phosphorus substituent a distinction between bent and linear phosphinidene complexes can be made. Bent phosphinidene complexes are characterized by very large ^{31}P NMR chemical shifts ranging from 660 ppm for W-**10** to 970 ppm for nickel phosphinidene **12**.



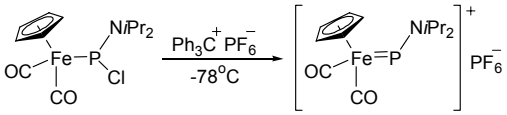
Scheme 5 – Examples of stable phosphinidene complexes and selected reactions.

The reactivity of these nucleophilic phosphinidene complexes has only little been explored, which might correspond to a limited reactivity, perhaps due to the steric bulk required to isolate these

compounds.[6] Of all stable phosphinidene complexes zirconocene phosphinidene **11** has been studied most thoroughly and was found to displace the halogens of organic halides, thus enabling access to phosphiranes and other phosphorus heterocycles.[32] Reaction with aldehydes resulted in phospha-alkenes and a four-membered metallocycle was formed upon reaction with acetylene.[33] Nickel phosphinidene **12** reacted with phenylacetylene to form metallabicyclobutane **16**, of which the uncomplexed phosphirene could be liberated using CO.[34] Group-transfer to ethylene took place leading to phosphirane **15** via an intermediate metallacycle, which could be identified spectroscopically.

1.2.2 Cationic Electrophilic Phosphinidene Complexes

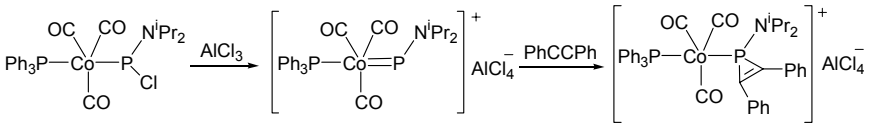
In 1984 Gladysz, Bertrand and co-workers reported spectroscopic evidence for a cationic phosphinidene complex of the type [RP=ML_n] in the reaction of iron-complex **17** with Ph_3CPF_6.[35] A down-field shift at 954 ppm was seen in the ^{31}P NMR, attributed to phosphinidene complex **18**, a value that would later be proven to be typical for a phosphinidene complex (Scheme 6). The complex could not be isolated and it was proposed to be thermally instable, giving insertion into the amino-substituent on warming up.



Scheme 6 – The first report of a phosphinidene complex.

More than twenty-five years later, using an identical approach, Carty *et al.* were able to synthesize a range of stable, isolable cationic phosphinidene complexes coordinated to metals ligated to both a Cp-ligand and a number of carbonyls (M=W, Mo, Fe, Ru, Os).[36] They showed that iron phosphinidene **18** could be isolated and demonstrated its stability at 70°C. The previously reported instability was proposed to result from the sensitivity of phosphinidene **18** to traces of water.[36a]

These cationic phosphinidene complexes are characterized by a combination of both an electron-donating as well as electron-withdrawing ligands at the metal, and might display ambiphilic behavior, but due to their positive charge these phosphinidenes react in an electrophilic manner. Reaction with phosphines occured at the phosphinidene phosphorus, which is characteristic for electrophilic phosphinidene complexes[36c] and though the product of the reaction of the Mo and W-complexed phosphinidenes with diphenylacetylene was assigned to be a metalaphosphacyclobutene complex,[36d] the spectral data were later recognized to be more consistent with a phosphirene complex.[37]



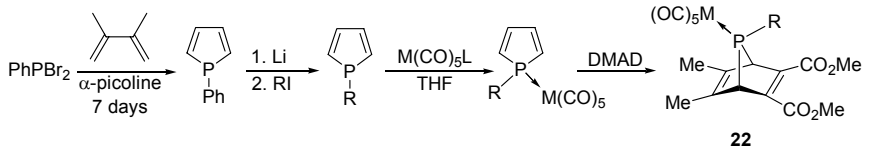
Scheme 7 – General rout to cationic phosphinidene complexes.

In the same fashion, reaction of $AlCl_3$ with chloro aminophosphine **19** yielded the stable cationic phosphinidene cobalt complex **20** (Scheme 7).[37] The σ-donating capacity of PPh_3 is less than that of a Cp-ring, so phosphinidene **20** reacted smoothly with diphenylacetylene to form the expected cationic phosphirene cobalt complex **21**. A cationic $Re(CO)_5$ phosphinidene complex was shown to react with azobenzene to form benzadiazaphosphole derivatives, presumably via attack on the electron-rich nitrogen.[38] Hence, these cationic phosphinidenes are the first examples of isolable electrophilic phosphinidene complexes.

1.2.3 Neutral Electrophilic Phosphinidene Complexes

So far neutral electrophilic phosphinidenes have remained elusive, though since their discovery by Mathey and co-workers in the early 1980s,[39] an impressing amount of research has been performed.[6, 40] The several approaches to these highly reactive species will be discussed separately.

Phosphanorbornadiene Complexes. The most common and most general method to generate neutral electrophilic phosphinidene complexes is the cheletropic elimination from 7-phosphanorbornadiene complexes **22**.[39] Whereas uncomplexed phosphanorbornadienes are unstable, after complexation the phosphinidene fragment is expelled at 110°C together with a phthalic acid diester as side-product. Addition of Cu(I)Cl lowers the reaction temperature to 55°C[39] but the reactive species is thought to be a copper-phosphinidene adduct, instead of a free phosphinidene complex.

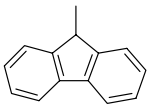
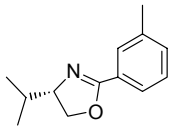
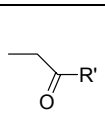
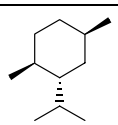
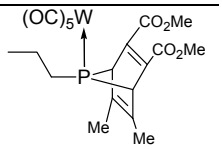


Scheme 8 – Synthesis of 7-phosphanorbornadiene complexes **22**. (DMAD=dimethylacetylenedimethylcarboxyalate)

Over twenty-five different substituents have been incorporated so far in the synthesis of phosphanorbornadiene **22** (Table 1). A drawback of this synthesis is the early introduction of the phosphorus substituent and the impossibility of application of amino-substituents, as the Diels-Alder reaction is hampered by side-reactions.[43] Amino-substitution of phosphiranes and phosphirenes would allow for easy functionalization.[41] Sterically demanding substituents retarded or prevented the last reaction step as well and in practice only complexation of phosphanorbornadiene **22** to group 6 metals (M=Cr, Mo and W) has been applied. However, the phosphanorbornadiene need not be

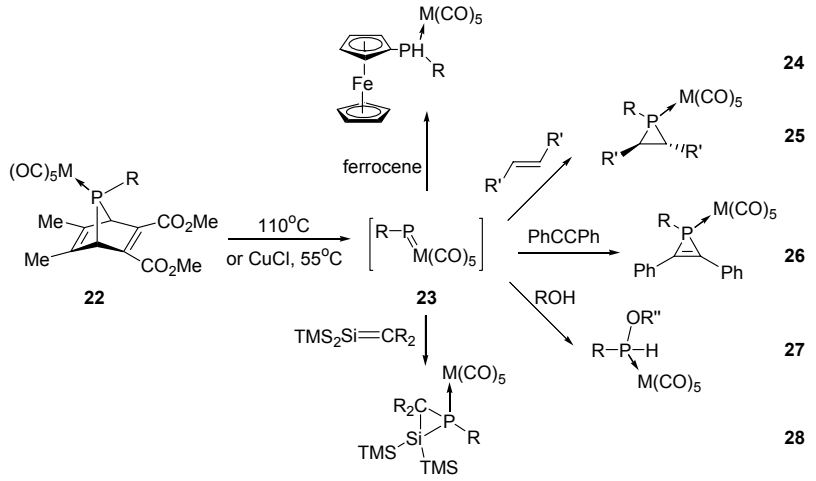
isolated to generate the phosphinidene: in the reaction of a phosphole-Fe(CO)$_4$ complex with DMAD in the presence of diphenylacetylene a phosphirene iron complex could be obtained, although in low yield (9%).[42]

Table 1 – Examples of substituents applied in the synthesis of **22**.

R						
Aryl	—Ph					
Ref.	39a	43	44			
Alkyl	—Me	—(CH$_2$)$_n$—	—(CH$_2$)$_n$—Cl			
		n=1-3	*n*=1-2	R'=Me, Et		
Ref.	39a	45	41, 46	43, 47	44	48
Others	—OMe			—F		
Ref.	49	43	43	49		

The reactivity of phosphinidene complex **23** is versatile and useful and the addition to unsaturated bonds takes a prominent role (Scheme 9). The addition to alkynes was the first reported synthesis of three-membered phosphirenes **26**.[39a] Addition to olefins provided a convenient entry to phosphirane complexes (**25**) and the formal [1+2] addition to C=X bonds resulted in novel three-membered heterocycles, like the first phosphasilacyclopropane **28**.[50] Insertion into activated H-bonds has commonly been observed (**27**) and the reaction with ferrocene is a beautiful example (**24**), indicating the high electrophilicity of [R-P=M(CO)$_5$].[51] Reaction of phosphinidene **23** with aromatic systems has not been observed, except for the addition to a highly strained [5]metacyclophane[52] and reaction with (guai)azulene.[53]

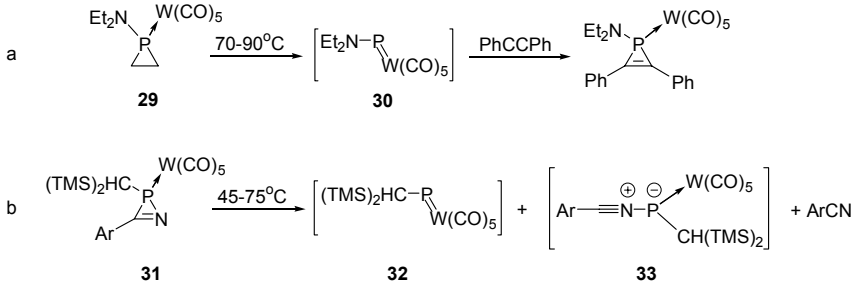
No spectral evidence has been obtained for phosphinidene **23** in any way, but several facts support the intermediacy of a phosphinidene complex. First, the addition to *Z*- or *E*-olefins proceeded with retention of stereochemistry, in accord with the concerted addition of a singlet species (see Scheme 9). Moreover, a kinetic analysis of the decomposition of **22** (R=Ph, M=W) proved it to be a first-order process, that only depended on the concentration of the phosphanorbornadiene **22**, and not on that of any substrate.[54] This is supportive of a phosphinidene generating mechanism, as addition of phosphinidene complexes to substrates is expected be have only a low energy barrier, or to proceed without barrier at all. [55- 56]



Scheme 9 – Decomposition of phosphanorbornadiene **23** and selected phosphinidene reactions.

In the presence of Cu(I)Cl a phosphinidene-copper adduct is believed to be the reactive species[55], which explains the sometimes different outcome of catalyzed phosphinidene reactions compared to uncatalyzed ones.[57] For the Cu(I)Cl-catalyzed addition of several substituted phosphinidenes to *p*-substituted styrene derivatives small negative Hammett constants could be determined, in accord with an electrophilic carbene-like intermediate.[58]

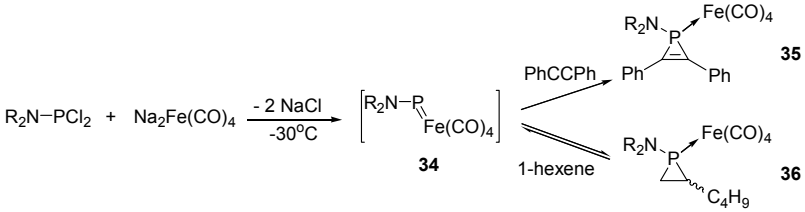
Retro-addition from Amino-phosphiranes and Azaphosphirenes. Free phosphinidenes can be generated by thermolysis or photolysis of phosphiranes. Complexed phosphinidenes have been generated by thermal retro-addition as well, but the required temperatures were generally high (>130°C), except for amino-susbstituted phosphiranes **29**. Under mild conditions (>70°C) these have been reported to yield the corresponding amino-phosphinidene complex **30**, which could be trapped with several reagents (Scheme 10a).[59] Though the reactions proceeded in high yields the method has a major draw-back: the synthesis of the amino-phosphirane complexes is complicated.



Scheme 10 – Phosphinidene generation by retro-addition.

Alternatively, phosphinidene complexes have been made availabe by retro-addition from aza-phosphirene complexes by Streubel and co-workers.[60] The temperature at which the phosphirene ring-system opens up is convenient (45-75°C), but prior to phosphinidene release a nitrilium phosphine ylid (**33**) is formed, whose formation leads to side-products in some cases. Moreover, aza-phosphirene complexes can only be synthesized with a large substituent.

Anionic Generation. Another method to generate phosphinidene complexes relies on the reaction of metal-dianions with dichloro phosphines. Huttner and co-workers suggested the intermediacy of a terminal phosphinidene complex in the reaction of $Na_2Cr_2(CO)_{10}$ with dichloro phosphines.[61] Likewise, King *et al.* proposed the formation of phosphorus-iron clusters occuring by way of [R_2N-P=$Fe(CO)_4$] (**34**) when reacting amino dichloro phosphines with $Na_2Fe(CO)_4 \cdot 1.5$ dioxane, a salt which is also known as Collman's reagent.[62]



Scheme 11 – Generation of an iron amino phosphinidene complex.

Lammertsma and co-workers were able to trap iron phosphinidene complex **34** at -30°C with acetylenes[63] and allenes,[64] but due to electron donation by nitrogen the electrophilicity of the phosphinidene complex is reduced (Scheme 11). For example, no reaction is observed with disubstituted olefins and the phosphiranes isolated in the reaction with terminal olefins are amenable to retro-addition at room-temperature. An elegant approach employs this lability by generating the phosphinidene in a terminal olefin (1-hexene) as solvent. After quantitative formation of phosphirane complexes **36**, the solution is filtered to remove sodium chloride. The consequent phosphirane-olefin solution can be used as a source of bottled [R_2N-P=$Fe(CO)_4$] and it can be stored for months without noticeable decomposition.[65]

Despite the fact that other metal-dianions can be used (Mo, W), the applicability of this anionic method is restricted to amino dichloro phosphines and a further limitation is posed by the experimental lability of most iron-amino phosphorus complexes, requiring careful purification procedures.

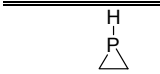
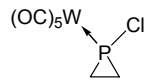
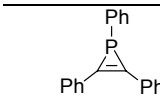
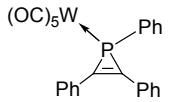
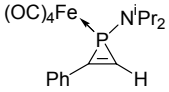
1.3 Phosphiranes and Phosphirenes

Of the phosphinidene reaction products the three-membered rings, both saturated and unsaturated, stand out. Though excellent reviews on these strained heterocycles are available[66] we wish to present some structural and physical data on phosphiranes and phosphirenes, because these heterocycles will frequently be encountered in these thesis and a good background knowledge will be helpful.

Phosphiranes are characterized by a small intracyclic CPC angle of 47-51°. A comparison of the available data shows that the phosphirane ring can 'breathe' easily, keeping the CPC angle remarkably constant, while the variation in the CP and CC bond-lengths is large 1.78-1.89 Å and 1.460-1.588 Å, respectively. The intracyclic CPC angle of *phosphirenes* is even smaller (42-46°), but again the three-membered ring is able to breathe and the P-C and C=C bond lengths vary in the ranges 1.71-1.82 Å and 1.30-1.36 Å, respectively.

The ^{31}P NMR chemical shifts of phosphiranes and phosphirenes are very characteristic: a very high-field shift compared to other tertiary phosphines is observed. Parent phosphirane holds the record, with its -341 ppm chemical shift, but even after complexation the chemical shift of phosphiranes is shifted to high-field (> -100 ppm). Due to the smaller CPC angle phosphirenes tend to resonate at higher field than comparable phosphiranes. The ring carbon resonances of phosphiranes are at high-field (0-30 ppm), similar to other three-membered rings and the proton resonances are shielded as well. Uncomplexed phosphiranes have large negative $^{1}J_{CP}$ coupling constants within the ring (33-82 Hz), as have uncomplexed phosphirenes, but complexation reduces the size of the coupling considerably to ca. 10-22 Hz. Table 2 displays structural and spectroscopic data of some representative examples.

Table 2 - Structural and spectroscopic data of selected phosphiranes and phosphirenes.

	L CPC (°)	*d* P-C (Å)	*d* C-C (Å)	δ ^{31}P NMR (ppm)	$^{1}J_{CP}$ (Hz)	Ref.
	47.4	1.867	1.502	-341	33.0	67
	49.2	1.78 1.81	1.49	-98	20	68
	41.8	1.820 1.821	1.299	-190	43.9	69
	42.8	1.790 1.787	1.307	-161	9.5	39a
	44.4	1.770 1.753	1.330	-48	21.8 (CPh) 0 (CH)	63

1.4 Scope and Outline of this Thesis

The preceding sections make clear that there is still much progress to make in phosphinidene chemistry. For example, free phosphinidenes have only been detected and determined in a few instances. Nucleophilic phosphinidene complexes have been synthesized, but their reactivity has been left unexplored to a large extent. Neutral electrophilic phosphinidene complexes have eluded isolation, in spite of, or perhaps because of, their high and useful reactivity. Also the diversity of electrophilic phosphinidene complexes is restriced to a few metals and they are only accessible using

a few methods. Consequently, the main objective of the research described in this thesis is to develop new approaches to phosphinidenes and electrophilic phosphinidene complexes, both to determine their existence, spectral properties and reactivity, as well as to develop new, simple and convenient ways of generation.

Chapter 2 will be devoted to a matrix-isolation and laser-flash photolysis study on a methylphosphirane tungsten complex. The aim of this study was the detection of an electrophilic phosphinidene complex under matrix-conditions, but this proved to be unsuccesful. The reaction-product after photolysis at 15 K is tentatively identified as the decarbonylation-product, which will be supported by calculated data.

Chapter 3 presents IR and UV/Vis data on matrix-isolated [MesP] which complements the EPR study by Gaspar. A laser flash photolysis study is shown to yield an identical UV spectrum and the reactions of the triplet phosphinidene will be discussed.

Chapter 4 expands the scope of the amino-phosphinidene iron complex by its intramolecular addition to double and triple bonds. In several cases the resulting bicyclic phosphiranes and phosphirenes are remarkably stable, but release the phosphinidene complex at room-temperature when a substrate is added. The intramolecular exchange of the phosphinidene moiety in an olefinic substituted phosphirane complex is shown by dynamic NMR experiments.

Chapter 5 presents the results of high-level ab initio calculations on the ring strain in small bicyclic N,P-heterocycles. In the research discussed in Chapter 4 several analogues were synthesized and the experimental observations will be correlated with the calculated strain energies.

Chapter 6 concerns with benzophosphepine complexes, which provide an excellent entry into phosphinidene chemistry. In this communication crystal structures of two benzophosphepines complexed to $W(CO)_5$ and to $Mn(CO)_2Cp$ will be shown. The reactivity of these complexes will be discussed and it will be shown that at 60-80°C phosphinidene complexes are expelled and can be trapped in very good yields.

Chapter 7 elaborates on benzophosphepine complexes, showing flexibility of the synthesis to variation of metals and substituents. The reactivity of several complexes is investigated and their decomposition subjected to kinetic analysis, which establishes a phosphinidene mechanism. Additionally, these benzophosphepines will be used to synthesize a novel ligand system.

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Chapter 2

A Matrix Spectroscopy and Laser Flash Photolysis Study of 1-Methyl Phosphirane Pentacarbonyltungsten

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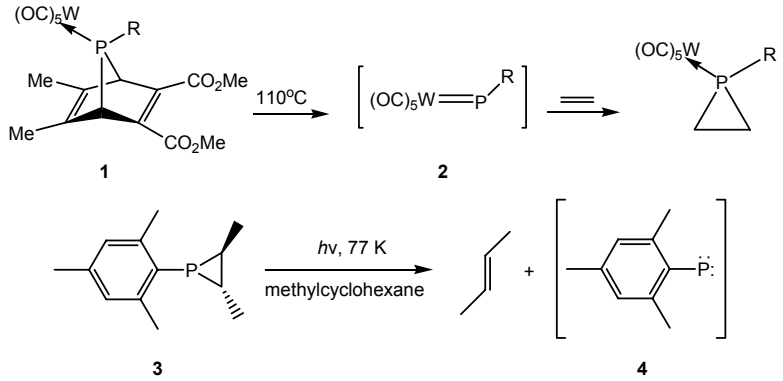
2.1 Introduction

Over the years phosphinidene complexes [R-P=ML_n] have developed from exotic compounds[1] to interesting and valuable reagents.[2] These phosphorus analogues of carbenes can be divided into two classes, either nucleophilic or electrophilic and similar to the distinction made for carbene complexes, these are called Schrock- or Fischer-type respectively. The ligands at the metal determine the philicity of the complex, as was shown by a bonding analysis study of a series of transition metal complexed phosphinidenes:[3] when the ligands are electron-donating (e.g. Cp) the phosphinidene complex shows nucleophilic behavior and consequently, when the ligands have electron-withdrawing capacity (e.g. CO) the phosphinidene complex is electrophilic.

Already numerous stable Schrock-type phosphinidene complexes with most of the transition metals have been reported,[4] often realized by inclusion of steric bulk in the molecule. However, this steric bulk hampers the reactivity of these nucleophilic complexes and only a few reactions are known.

From a synthetic point-of-view the Fischer-type phosphinidenes are much more interesting. For example, Carty *et al.* have reported on stable cationic electrophilic phosphinidene complexes which add to phosphines or may react with acetylenes to form cationic phosphirene complexes.[5] Yet, the transient phosphinidene complexes made available by Mathey in the early 80s[6] have been proven to be most valuable, as they add to a variety of unsaturated bonds and insert in activated C-H bonds.[7] Unfortunately, these neutral phosphinidene complexes of the form [R-P=M(CO)$_5$] (M=W, Mo or Cr) have remained elusive. Their existence has been inferred from trapping reactions and from kinetic analysis of the thermal decomposition of the precursor, 7-phosphanorbornadiene complex **1**,[6] of which the 1st order rate does not depend on the reactants.[8] This supports a phosphinidene forming mechanism, assuming that the rate is determined by 1,4-elimination of the phosphinidene followed by much faster addition to the trapping reagent or substrate. Theoretical studies have shown that singlet phosphinidene addition to double bonds proceeds almost barrierless in most cases.[9]



Scheme 1 - Methods of generation of phosphinidenes.

The lack of direct evidence for neutral Fischer-type phosphinidene complexes, like **2**, may be a result of the absence of an energy barrier, but this elusiveness is remarkable in view of the wide variety of known Fischer carbene complexes.[10] It has a parallel in the scarce reports on uncomplexed phosphinidenes in comparison to the large number of detections of free carbenes,[11] as the only evidence for free phosphinidenes is an EPR signal of 2,3,5-trimethylphenylphosphinidene **4** (MesP) at 15K in frozen cyclohexane glass, generated by photolysis of mesitylphosphirane **3**[12] and a matrix-IR study on H_3SiP, generated by the reaction of atomic silicon with phosphane.[11] Indeed, the two main techniques used to identify reactive intermediates like **2** are matrix isolation, as well as laser flash photolysis (LFP). Given the large number of reactions attributed to [R-P=W(CO)$_5$] (**2**) both in our group and elsewhere, we set out to determine this reactive intermediate using these techniques and we will describe both shortly.[13]

The study of short-lived intermediates can be approached in two ways. One way is to adjust the experimental conditions to increase the lifetime of the intermediate to the extent where its detection becomes possible with standard spectroscopic techniques. This is accomplished by matrix isolation. The other approach is to study the reaction under normal laboratory conditions, but accelerate the detection techniques in such a way that the behavior of the intermediate can be adequately monitored. Laser flash photolysis is one technique to do this. In fact, the invention of the laser in the early 1960s provided the opportunity for a fast generation of the intermediate as well, which is just as essential for fast detection. The 1967 Nobel prize was awarded to Norrish, Eigen and Porter for their contributions to the development and application of flash photolysis. Almost thirty years later Zewail received the 1999 Nobel prize for the development and application of laser flash photolysis into the femtosecond time-frame.

2.1.1 Matrix isolation

Generally speaking, matrix isolation refers to a range of techniques where guest molecules are prevented from diffusion by trapping them in rigid host materials. In a more stricter sense, matrix isolation applies to a procedure in which a substrate is mixed with a large excess of an inert host gas. The mixture is condensed on a surface which is cold enough to assure rapid solidification of the material. The aim is to have each substrate molecule surrounded by one or more layers of unreactive host material.

The matrix or glass is irradiated at cryogenic temperatures in order to form the reactive intermediate which can be analyzed by regular spectroscopic techniques, like IR and UV. A range of follow-up experiments can be envisioned, like secondary photolysis or annealing of the matrix leading to bimolecular reactions, which is especially informative if the matrix is poisoned with a trapping reagent from the start.

However, matrix isolation has its limitations. The first and most important one is that the precursor has to be volatile and that deposit on the surface can be performed without decomposition. Another limit can be encountered when precursors that are known to provide reactive intermediates in solution or the gas phase do not yield enough of the intermediate in the matrix as a result of the *cage effect*. Usually all the fragments formed upon cleavage of the precursor remain trapped in the matrix cage, except for hydrogen or fluorine atoms. Consequently, recombination of the fragments is always a possibility and may occur either as a result of low-barrier thermal processes or photochemical activation. Another problem is the low heat capacity of noble gasses. Excess energy in the generation process of the reactive intermediate is not likely to be transferred to the matrix, but may be imparted on the intermediate, leading to secondary chemical processes, which make it impossible to generate the primary reactive intermediate.

2.1.2 Laser flash photolysis (LFP)

Laser flash photolysis is the generation of a reactive intermediate from a precursor by a high-energy laser pulse and nano-second detection of fluctuations of one of the characteristics of the precursor (usually absorbance) before and after the laser flash. The advantage of LFP is the study of the reactive

intermediate under the normal reaction conditions and the possibility to obtain kinetic data, but the quality of spectral data is usually lower than the data obtained by matrix isolation.

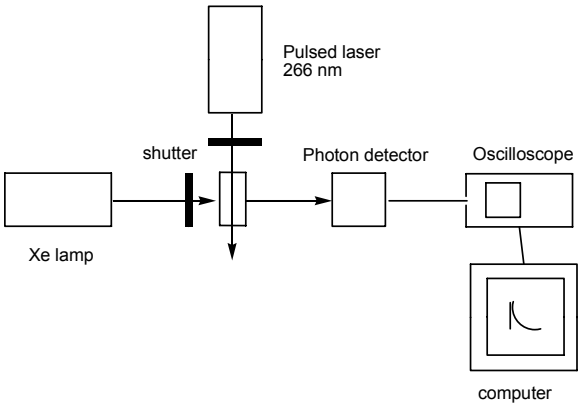


Figure 1 - Set-up of a laser flash photolysis experiment.

In a representative laser flash photolysis set-up (see Figure 1) a dilute solution of the precursor, flowing through the cuvet, is hit by the laser pulses at regular intervals and the photon-detector measures the absorbance difference of the Xe lamp before and after the laser flash. The decay of the absorbance measured at a fixed wave-length, or the absorbance at different wave-lengths and different time intervals is recorded, generating an UV/Vis spectrum of the transient species. Again trapping or quenching reactions can be investigated.

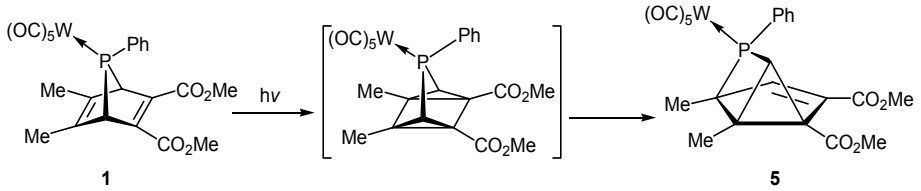
2.1.3 Computational Investigation

Spectral data alone would often be insufficient to determine the nature of the intermediate. Therefore, the experimental spectra acquired by both techniques should be compared to theoretical data to establish which intermediate(s) are formed. The prediction of IR spectra by DFT methods has become a standard tool. Vibrational analysis using the harmonic approximation yields in most cases good agreement with the experiment. The work of Scott and Radom showed the B3LYP /6-31G* level to work especially well for prediction of IR spectra. Due to the application of the harmonic approximation a scaling factor is required, which was derived by least-square fitting based on a large set of test-molecules.[14]

For the prediction of UV/Vis spectra reliable calculations of excited-state energies and transition moments (i.e. the strength of the absorption) are needed which require usually considerable effort. A correct description should include multiconfigurational wave functions thus limiting the size of the system to be studied, and dynamic electron correlation effects in excited states should be accounted for, which increases computational size as well. A different approach is to look at the response of the ground-state electron distribution to oscillating electric fields of different frequencies. This can be performed with time dependent-DFT, which is implemented in the Gaussian series of programs and is used increasingly and successfully, though its reliability is not firmly grounded yet.

2.2 Experimental Results

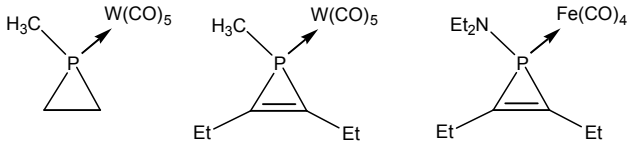
For the detection of an eletrophilic phosphinidene complex we had to find a suitable precursor for phosphinidene **2**. 7-Phosphanorbornadiene **1** could not be used for a photochemical generation of the phosphinidene as its norbornadiene skeleton rearranges under the influence of light, presumably via a phosphaquadracyclane to tricyclic **5**.[15]



1 **5**

Scheme 2 - Rearrangement of 7-phosphanorbornadiene **1** under solar light.

Since several examples of phosphinidene generation by photolysis of phosphiranes are known,[16] and phosphirane complexes expel phosphinidenes at elevated temperatures, we chose methyl phosphirane complex **6** (Chart 1) to study its behavior under matrix and laser flash photolysis conditions, hoping to determine phosphinidene [Me-P-W(CO)$_5$]. Sublimation of **6** proceeds easily at lower pressures, so deposition on the surface should be possible.



6 **7** **8**

Chart 1 – The phosphinidene precursors used.

Methyl phosphirane tungsten(0)pentacarbonyl (**6**) was synthesized by reaction of methyl-7-phosphanorbornadiene complex **1** with ethylene in 74% yield. A room-temperature IR spectrum (KBr) showed the CO stretching frequencies at 2074 and 1930 cm^{-1}.

2.2.1 Matrix isolation

A dilute mixture of **6** in argon was deposited on a cold CsI window and cooled to 15K. In the argon matrix the CO absorptions appeared at 2080 cm^{-1} and at 1952 cm^{-1} and a small shoulder was visible at 1960 cm^{-1}. Upon extended irradiation (254 nm) of matrix isolated **6** a difference IR-spectrum was obtained (Figure 2). As can be seen phosphirane CO-absorptions were depleted and four new ones were formed at 2040 (m), 1925 (s), 1910 (ms), 1895 (s) cm^{-1}, together with a small but significant amount of free CO (2139 cm^{-1}).

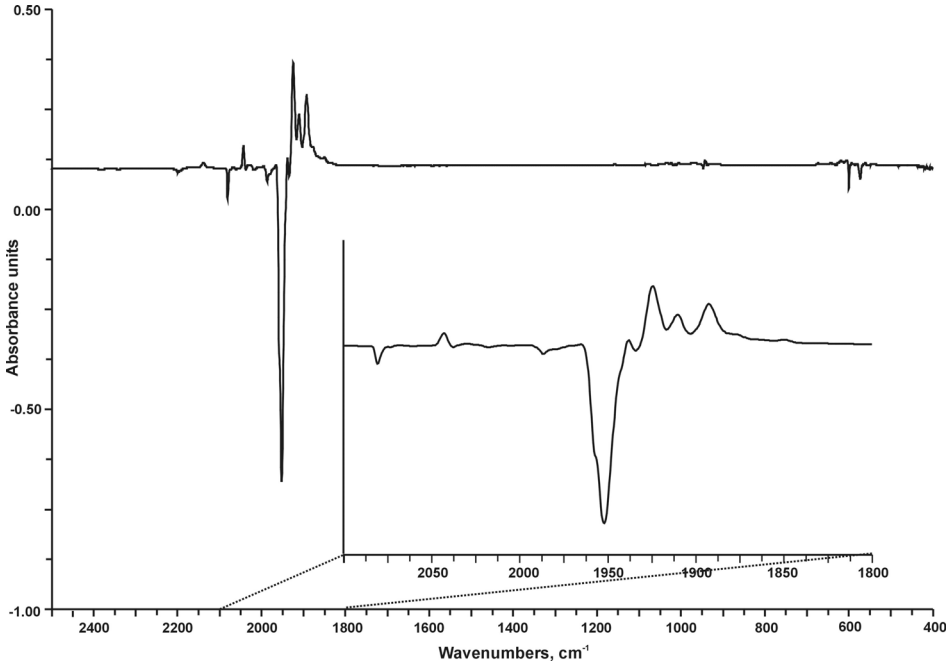


Figure 2 – Difference IR spectrum (Ar, 10 K) of the spectra obtained after photolysis of **6** at λ_{exc} = 254 nm. Absorptions pointing down belong to **6**, absorptions pointing up belong to the photoproduct. Inset: CO region.

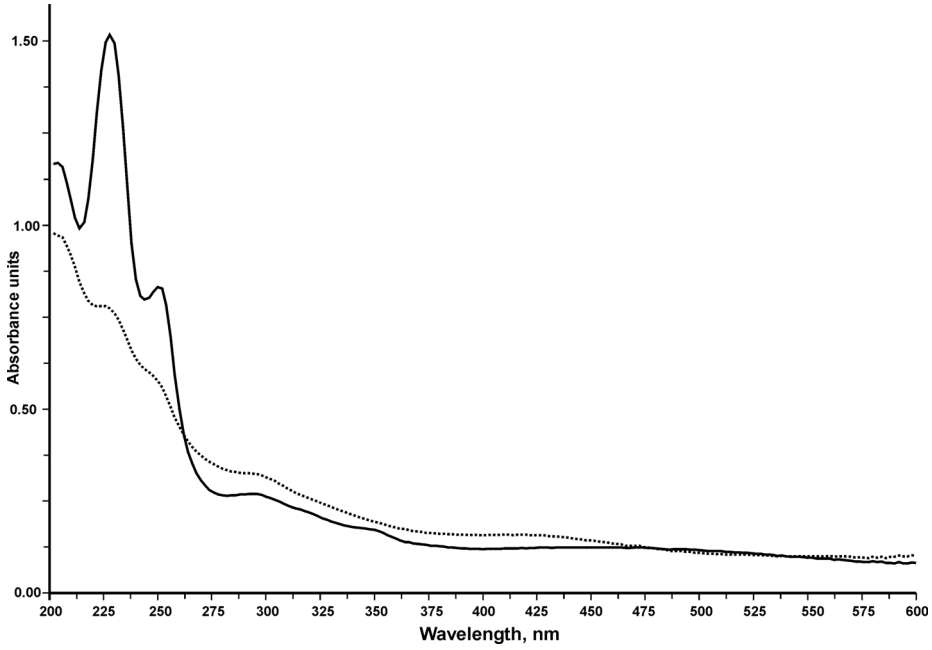


Figure 3 – UV/Vis spectra (Ar, 10K) of **6** before (solid) and after 254 nm photolysis (dashed).

The UV/Vis spectrum of matrix-isolated phosphirane **6** showed intense absorptions at λ =200, 225 and 250 nm. (figure 3). After irradiation at 254 nm these absorptions had decreased, while two other absorptions (300, 380-450 nm) had grown in intensity. Subsequent radiation with λ = 420-450 nm regenerated the IR and UV absorptions belonging to phosphirane **6** and in the IR spectrum free CO disappeared as well. Warming up of the argon matrix after 254 nm photolysis to 30K did not lead to any change in the difference spectrum. Doping the matrix with either 1-2% HCl or with oxygen and warming up to 42K did not affect the results. From the latter observation it can be concluded that a triplet species was not formed. Photolysis of **6** in a pure CO matrix led to a photoproduct with one single CO frequency attributed to $W(CO)_6$.[17]

The same photochemical behavior was found for phosphirane **6** in a xenon matrix: the phosphirane CO absorption pattern was virtually the same as in argon, but the frequencies of the photoproduct shifted to lower wavenumbers by about 10 cm^{-1}. However, upon irradiation with λ = 420-450 nm the phosphirane was regerenated, now without full depletion of the signal assigned to free CO, which could imply that decarbonylation is not the only process taking place.

2.2.2 Laser flash photolysis

Laser flash photolysis of phosphirane **6** dissolved in cyclohexane led to the formation of a transient species which showed 2nd order decay with a rate constant of $8.5x10^3$ l mol^{-1} s^{-1} and a life-time of 55 µs (Figure 4). The transient species (λ_{max}= 415 nm) was quenched by several substrates (Table 1) and a strong steric effect was observed. For example, the smaller *n*-propylamine quenched the transient about three times faster as the larger triethylamine. Noticeably, LFP of phosphirane **6** in 1-hexene did not lead to a significant decrease in life-time of the intermediate, as would be expected for a highly reactive transient phosphinidene that adds barrierless to double bonds.

Since the experiments described above seemed insufficient to reach a definitive conclusion about the nature of the transient species, other precursors were analyzed as well, though less extensively than **6** (see Chart 1). Phosphirene **7** proved to be photochemically active in an argon matrix and irradiation of matrix isolated **7** resulted in a similar pattern of CO frequency absorptions as found for the photoproduct of **6**, but all are at somewhat different positions (see Figure 5, **6** vs. **7**: 2040 vs. 2038 cm^{-1}, 1925 vs. 1933 cm^{-1}, 1910 vs. 1919 cm^{-1} and 1895 vs. 1886 cm^{-1} and an additional band at 1903 cm^{-1}). Also in this case free CO was formed as evidenced by the small absorption at 2138 cm^{-1} (vs. 2139 cm^{-1} for free CO after photolysis of **6**). Phosphirane **6** and phosphirene **7** could serve as precursors for the same phosphinidene complex [Me-P=$W(CO)_5$]. The similarity of the IR data indicates a similar photoproduct, but for the phosphinidene complex to have been formed, they should have been identical.

Iron-complexed phosphirene **8** was photochemically inactive under matrix conditions: only a small amount of CO was observed after 48h irradiation (254 nm).

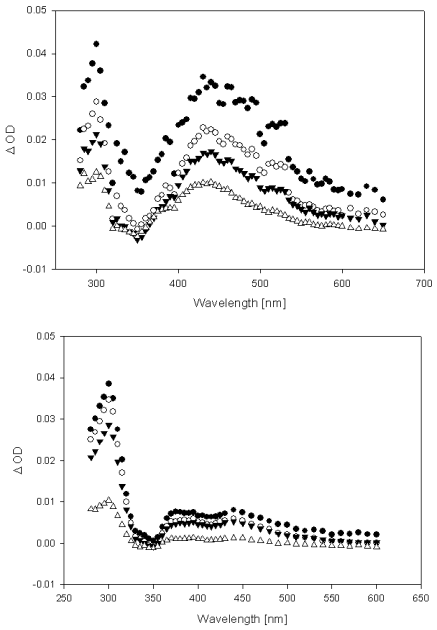


Table 1 – Rate constants of the reaction of transient formed after LFP with several substrates.

Quencher	k (10^6 l mol^{-1} s^{-1})
Tetramethylethylene	3.9
1-Octene	3.5
1-Octyne	6.1
Methanol	47
THF	4.6
Diethylamine	7.4
Triethylamine	4.5
n-Propylamine	13
n-Dodecyl mercaptane	21
Acetonitrile	75
Cyclohexyl isocyanide	73

Figure 4 – UV/Vis spectrum of the transient in cyclohexane generated by a laser flash of 266 nm, measured after several *t* (top). *t* = 50 ns (●), 3 μs (○), 10 μs (▼), 40 μs (△).Similar, but in the presence of methanol (bottom).

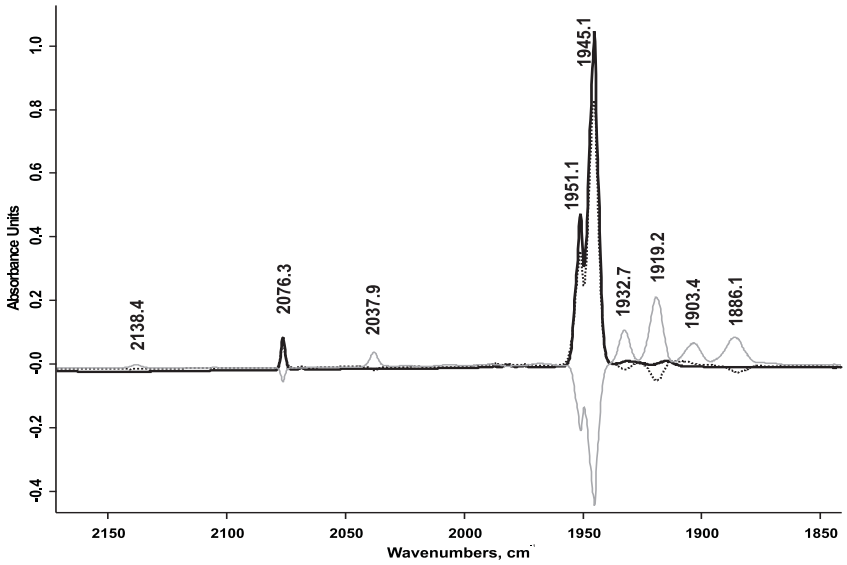


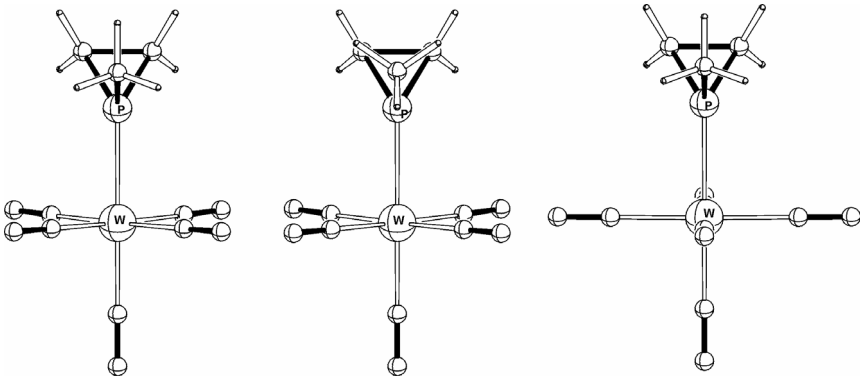
Figure 5 – IR spectrum of phosphirene **7** in Ar matrix (solid black line); differential IR spectrum obtained after photolysis (2h) of **7** at λ_{exc} = 254 nm (grey line); difference IR spectrum obtained after photolysis (7 min) with λ = 385-420 nm (dotted line).

2.3 Calculations and Discussion

Phosphirane **6** is photochemically active under matrix isolation and in the laser flash photolysis. The experiment shows a large shift of ~40 cm^{-1} to lower wavenumbers for all CO frequencies upon irradiation of phosphirane **6** and therefore, in the discsussion we will focus on these frequencies, especially because these are the most intense ones and may serve as a fingerprint. Only where necessary other absorptions will be included. As mentioned in the introduction the B3LYP functional combined with the 6-31G* basis-set usually gives reliable results. To account for relativistic effects we will use the LANLD2Z basis-set and ECPs for tungsten.

The lowest-energy conformation of the phosphirane **6** is shown in Table 2 and the binding energy of phosphinidene [MeP=$W(CO)_5$] to ethylene is calculated to be –42.2 kcal/mol. Both the phosphirane and the methyl-group adopt a staggered position with respect to the $W(CO)_5$ fragment and also with respect to each-other (**A**). Eclipsing of hydrogens leads to a transition state (**B**) 1.7 kcal/mol higher in energy, identified by an imaginary frequency (-168 cm^{-1}) and rotation around the P-W bond leads to the second minimum structure (**C**) which is calculated to be of virtually the same energy as **6A**.

Table 2 - Conformations of **6**, energies and calculated CO frequencies.



6A – -42.2 **6B** – -40.5 **6C** – -42.0

ν_{CO}	**6A**		**6B**[a]		**6C**	
Experimental	Calcd	Scaled[b]	Calcd	Scaled[b]	Calcd	Scaled[b]
2080 (m)	2150 (*189*)	2067	2150 (*190*)	2067	2151 (*192*)	2068
1960 (sh)	2048 (*940*)	1969	2047 (*939*)	1968	2048 (*929*)	1969
1952 (s)	2041 (*1937*)	1962	2041 (*1952*)	1962	2045 (*1948*)	1966
	2041 (*1878*)	1962	2041 (*1884*)	1962	2038 (*1880*)	1959

B3LYP/6-31G*/LANL2DZ. All values in kcal/mol (E) or cm^{-1} (frequencies). Energy relative to phosphinidene **9A** and ethylene. Calculated intensity in parentheses. [a] Conformer **6B** is not a minimum structure, (ν_{im}=-168 cm^{-1}, C-P rotation). [b] Frequencies scaled by 0.9614.[14]

In the experimental IR spectrum of phosphirane **6** only three CO absorptions are present, which shows that local C_{4v} symmetry can be imposed on the $W(CO)_5$ fragment. In that case, it possesses two allowed modes, a_1 and e, in which the a_1 mode is responsible for two vibrations, (2080 cm^{-1} and 1960 cm^{-1}) and the e mode for the vibration at 1952 cm^{-1}.[17] The calculated CO-frequencies appear to depend only little on the exact conformation, though the degeneracy of the e mode is lifted in the case of **6C**. Scaling of the frequencies with the recommended scaling factor[14] results in a reasonable agreement: the highest calculated frequency is 13 cm^{-1} too low, whereas the three other frequencies are calculated to be 9-10 cm^{-1} higher than the experimental values.

Reoptimization of global minimum **6A** with the BP86 functional results in unscaled CO frequencies comparable to the scaled B3LYP ones. Scaling with the recommended scaling factor for BP86/ 6-31G* calculations (0.9914)[14] does lead to a better agreement for the three lower vibrations, but results in a $\Delta\nu_{exp\text{-}calc}$ of 32 cm^{-1} for the highest frequency. Since the scaling factor is almost unity, and because we use the LANL2DZ basis-set for tungsten we chose to use the unscaled BP86 frequencies throughout.

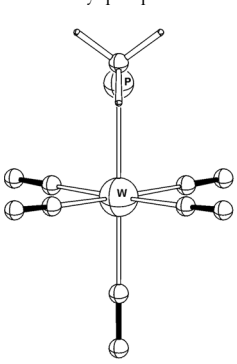
Table 3 - ν_{CO} **of 6A** with BP86/6-31G*/LANL2DZ. Scaling by 0.9914. Calculated intensities in parentheses.

Exp.	Mode	Calculated	Scaled
2080 (m)	a_1	2066 (*181*)	2048
1960 (sh)	a_1	1975 (*756*)	1958
	e	1964 (*1607*)	1947
1952 (s)	e	1964 (*1557*)	1947

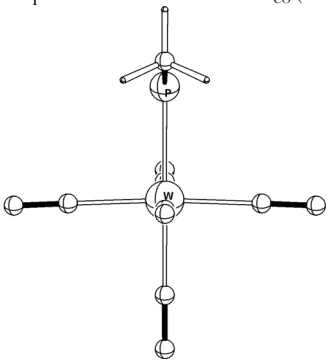
Next, several conformations of phosphinidene complex **9** were calculated and analyzed. Again, there is little difference between eclipsed and staggered conformations (~0.9 kcal/mol), but there appears to be only one minimum (**9A**) (Table 4). All other conformations are identified to have at least one imaginary frequency. Though the phosphinidene is a $W(CO)_5$ species four different CO absorptions are calculated, which implies the local C_{4v} symmetry is broken, perhaps caused by hindered rotation of the W-P bond. The number of absorptions and their intensities have some likeness to those of the photoproduct, but the wavenumbers do not match very well, even after scaling being off by ca. 60 cm^{-1}. Moreover, the three lowest frequencies are shifted by about 20 cm^{-1} to *higher* wave-numbers compared to those of phosphirane **6**, while the highest a_1 absorption remains virtually unchanged ($\Delta\nu$ = 8 cm^{-1}). This is understandable, as formation of a phosphinidene complex from **6** affects the $W(CO)_5$ fragment only indirectly, as the reaction occurs at the phosphirane moiety.

To evaluate the effect of the matrix atoms on the electrophilic phosphinidene complex, complex **9B** was re-optimized in the presence of two argon or xenon atoms (Stuttgart basis-set[18]) at confined distances (3.2 and 3.5 Å for argon, 3.5 and 3.8 Å for xenon) and angles (90° or 100°). These restrictions were necessary as simple optimization led to a moving apart of the noble gas atoms and the phosphinidene. The more severe the restrictions the larger the decrease of the wave-numbers, probably as a result of a bending of the carbonyls (see table 5). Still, the general effect on the vibrations is too small to assign phosphinidene complex **9** to the photoproduct.

Table 4 - Methyl phosphinidene tungsten complexes **9A-B** with calculated ν_{CO} (cm^{-1}).



9A – 0.0 kcal/mol

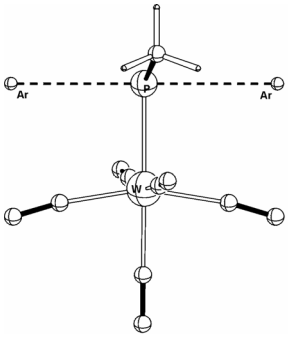


9B – 0.9 kcal/mol

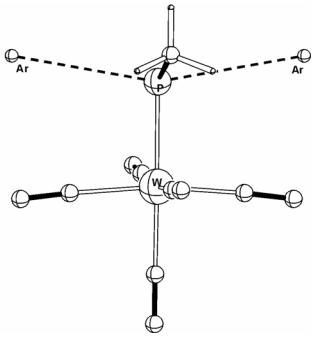
Photoproduct	Calc. 9A	Scaled[a]	Calc. 9B[b]	Scaled[a]
2038 (m)	2074 (*260*)	2056	2075 (*253*)	2057
1925 (s)	1993 (*696*)	1976	2001 (*1470*)	1984
1910 (ms)	1988 (*1539*)	1971	1989 (*720*)	1972
1895 (s)	1986 (*1419*)	1969	1976 (*1437*)	1959

BP86/6-31G*/LANL2DZ.[a] Scaled by 0.9914. [b] ν_{im}=-96. Calculated intensities in parentheses.

Table 5 – Phosphinidene **9B** optimized in the proximity of two argon atoms. **I** $d_{Ar\text{-}P}$ = 3.2 Å, *L* Ar-P-W=90°. **II** $d_{Ar\text{-}P}$=3.5 Å, *L* Ar-P-W=100°.



I – 10.8 kcal/mol



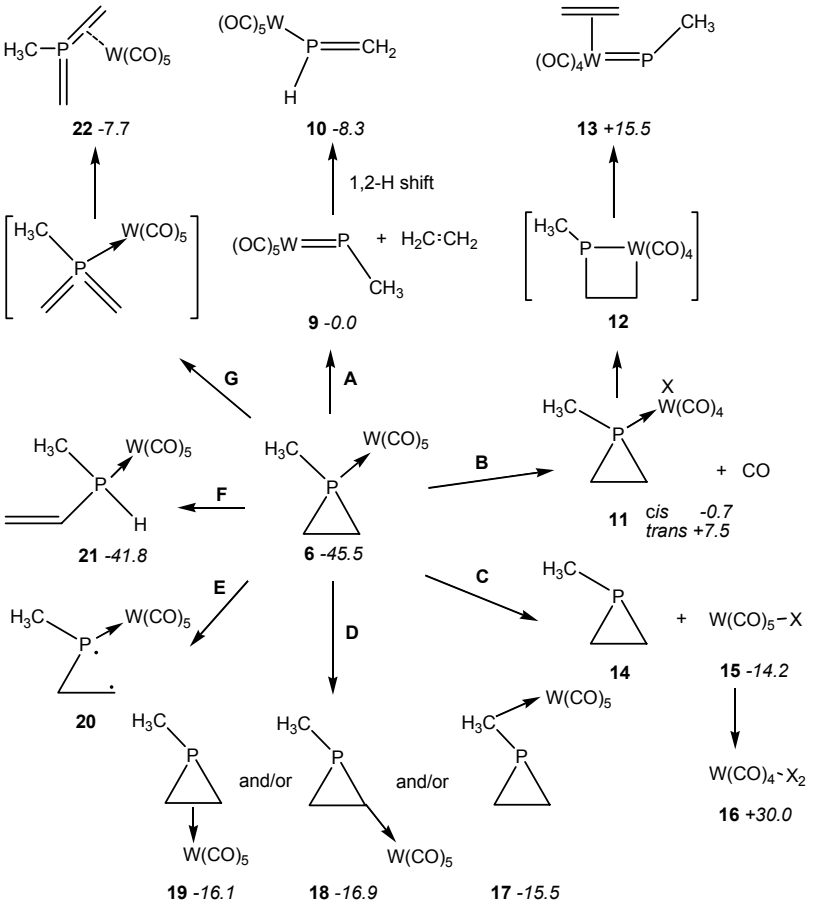
II – 3.1 kcal/mol

Photoproduct	Calc. 9B-I	Scaled[a]	Calc. 9B-II	Scaled[a]
2038 (m)	2066 (*349*)	2049	2072 (*283*)	2054
1925 (s)	1985 (*711*)	1967	1993 (*1520*)	1975
1910 (ms)	1984 (*1474*)	1968	1988 (*737*)	1970
1895 (s)	1973 (*1352*)	1956	1977 (*1393*)	1958

BP86/6-31G*/LANL2DZ/Stuttgart. [a] scaled by 0.9914. Calculated intensities in parentheses

Moreover, the experimental data give no convincing evidence for the formation of a phosphinidene complex. First of all, a phosphinidene complex is expected to be much more reactive, capable of reaction with HCl at low temperatures. Also, in the LFP experiment the spectrum does not change much from cyclohexane to 1-hexene, as would be expected for a highly reactive transient phosphinidene that adds almost barrierless to double bonds. Finally, for photolysis of phosphirane **6** and phosphirene **7** to result in a phosphinidene complex, both matrix experiments should have produced identical IR spectral data after photolysis. This is not the case and the similarity of the absorption patterns of both photoproducts suggest a similar, but different photoproduct, in which the phosphirane carbons are still attached to the metalfragment.

Thus, the question about the identity of the photoproduct remains and the possible reaction pathways are summarized in scheme 3.



Scheme 3 - Possible reactions on photolysis of phosphirane **6** and calculated energies (italics) relative to phosphinidene **9A** (BP86/6-31G*/LANL2DZ/Stuttgart).

There are several experimental facts which give significant clues to the nature of the photoproduct. First, free CO is formed, which indicates decarbonylation (path B) takes place. Secondly, the CO absorptions of the photoproduct are shifted to lower wave-numbers (red-shift) compared to phosphirane **6** by ~40 cm^{-1} and the number of absorptions increases from three to four. The number of absorptions corresponds to a *cis*-$W(CO)_4LL'$ species with local C_{2v} symmetry. The size of the frequency shift points toward a change in the coordination sphere of the metal and its direction to lower wave-numbers signifies that the remaining carbonyls are weaker bound to the metal. It has been shown for $W(CO)_5L$ complexes that a strongly electron accepting ligand L increases the amount of backbonding from the metal into the π*-anti-bonding orbital of the *trans* carbonyl ligand and consquently lengthens the *trans*-CO bond.[19] Similar reasoning would suggest that photochemical expulsion of one of the carbonyls of the $W(CO)_5$ fragment in phosphirane **6** leads to longer metal-CO bonds and hence to a red-shift.

This is confirmed by the data shown in table 6. Complexation of the vacant site of $W(CO)_5$ to an argon atom results in a shift of 2 cm^{-1} for the highest a_1 mode, which is dominated by the axial carbonyl stretch. This is consistent with the previously reported lengthening[20] of the axially bound carbonyl bond length upon noble gas coordination of a $M(CO)_5$ fragment.[21] Release of a second carbonyl causes a further sizable red-shift (23-34 cm^{-1}) while the number of bands increases from three to four (Table 6b). The increased amount of back-donation results in a lengthening of the remaining CO bonds: whereas the calculated CO bond lengths in $W(CO)_5$ are 1.174 Å (axial) and 1.167 Å (equitorial) these increase to 1.178 and 1.170 Å in C_{2v} $W(CO)_4$.

Table 6a – Calculated CO frequencies for several $W(CO)_5$ species, L = phosphirane.

Exp.	$W(CO)_5$	$W(CO)_5Ar$ (**15**)	$W(CO)_5L$ (**6A**)	Mode
2038	2082	2080	2066	a_1
1925	1977	1974	1975	e
1910	1977	1974	1964	e
1895	1965	1967	1964	a_1

Table 6b – Calculated CO frequencies for several C_{2v} $W(CO)_4$ species, L = phosphirane and comparison of calculated and experimental modes of $W(CO)_4Ar_2$ (**16**) and of the experimentally reported vibration modes for C_{2v} $W(CO)_5L^1L^2$ species.

Exp.	$W(CO)_4$	$W(CO)_4Ar_2$ (**16**)		$W(CO)_4L$	$W(CO)_4ArL$ (*cis*-**11**)	$W(CO)_4L^1L^2$ [a]
2038	2048	2044	2053	2031	2030	2025-2065
1925	1954	1953	1939	1955	1954	1930-1940
1910	1953	1946	1926	1939	1937	1910-1925
1895	1933	1933	1894	1932	1933	1870-1895
	calc.	*calc.*	*exp.*	*calc.*	*calc.*	*exp.*

BP86/6-31G*/LANL2DZ/Stuttgart. Frequencies in cm^{-1}. [a] The frequencies are based on a comparison of availabe data of known C_{2v} $W(CO)_4$ species.[17]

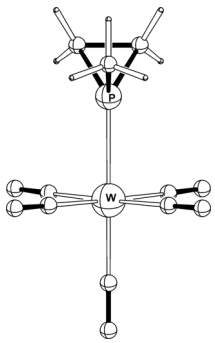
Coordination of the vacant sites of $W(CO)_4$ to argon (**16**) results in a slight decrease of the calculated absorptions and finally, replacement of an argon atom by a better electron accepting phosphirane ligand (*cis*-**11**) leads to a further decrease of the calculated absorptions.

The agreement between the calculated and experimental IR frequencies of decarbonylation product *cis*-**11** (path B, scheme 3) appears to be only moderate, but this may be attributed to a qualitative inaccuracy of the calculations. A comparison of the calculated CO frequencies of $W(CO)_4Ar_2$ (**16**) with those experimentally reported[17] shows a similar discrepancy as between *cis*-**11** and the photoproduct (see table 6b). Moreover, when the frequencies of the photoproduct are compared to those experimentally found for other $W(CO)_4$ species the formation of *cis*-**11** is highly plausible. Additional support is given by the many reports on photo-initiated carbonyl-dissociation from $PR_3W(CO)_5$ and other $W(CO)_5$ precursors under matrix conditions, of which some even date back to the 1970s.[17, 22, 23]

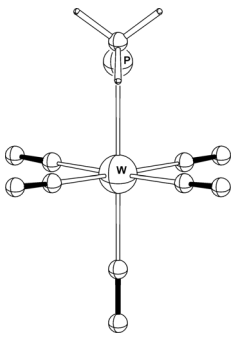
Apart from equitorial CO dissociation resulting in *cis*-**11**, axial dissociation leading to *trans*-**11** is possible as well. When local symmetry is applied *trans*-**11** can be expected to yield three CO frequencies, which are calculated to coincide with those of *cis*-**11** (Table 7). We cannot exclude the formation of *trans*-**11**, but it is unlikely, as a computational study showed that due to the weak π-acceptor ability of the phosphine group the equitorial carbonyls are weaker bound than the axial CO.[24] Our calculations reflect the preference for equitorial dissociation, since dissociation of the axial CO leads to a 8.2 kcal/mol less stable structure than *cis*-**11** (Table 7).

Table 7 – Representation of reaction products upon photolysis of methylphosphirane-$W(CO)_5$ (**6**), their energies (kcal/mol) relative to phosphinidene **9A** and the ν_{CO}, and if present ν_{PH} (cm^{-1}). (BP86/6-31G*/LANL2DZ/Stuttgart)

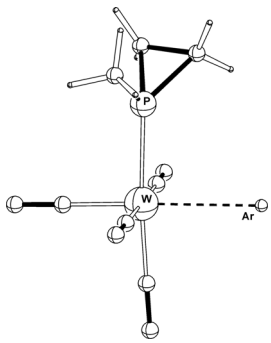
	6A	**9A**	**10**	***trans*-11**	***cis*-11**	**15**	**16**
Rel. E	-42.2	0.0	-8.3	+7.5	-0.7	-14.2	+30.0
Exp.			2373 (w)				
2038 (m)	2066 (w)	2074 (w)	2075 (w)	2030 (w)	2030 (w)	2080 (vw)	2043 (vw)
1925 (s)	1975 (m)	1993 (m)	1985 (ms)		1954 (m)	1974 (s)	1952 (w)
1910 (ms)	1964 (s)	1988 (s)	1985 (s)	1932 (s)	1937 (s)	1974 (s)	1947 (s)
1895 (m)	1964 (s)	1986 (s)	1975 (s)	1931 (s)	1933 (m)	1967 (m)	1932 (m)



6A



9A

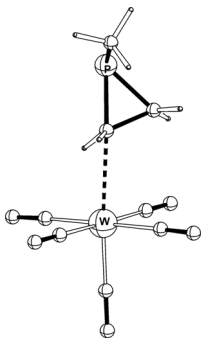


***cis*-11**

There are two experimental facts which seem to question that decarbonylation is the predominant process. First, irradiation of the photoproduct with $\lambda > 420$ nm in a xenon matrix led to reformation of the phosphirane while the signal of free CO seemed to remain intact. However, the intensity of the free CO signal at 2139 cm^{-1} is very weak in all cases (see e.g. Figure 2 and Figure 5). Whereas the calculated intensity of the CO vibration is 56, the intensities of the metal-carbonyl vibrations are 30-100 times larger. As a result, it is difficult to judge the proportionality of the carbonmonoxide formation relative to the photoproduct, and also, if it decreases proportionally in the xenon matrix.

Table 7 (Continued)

17	18	19	21	22	13a	13b
-15.5	-16.9	-16.1	-41.8	-7.7	+15.5	+18.6
			2361 (vw)			
2075 (w)	2074 (w)	2072 (w)	2065 (w)	2058 (w)	2047 (w)	2042 (w)
1972 (s)	1970 (s)	1965 (s)	1976 (s)	1990 (w)	1992 (w)	1979 (w)
1969 (ms)	1967 (ms)	1964 (s)	1963 (s)	1968 (m)	1975 (w)	1977 (w)
1966 (ms)	1966 (s)	1961 (m)	1961 (s)	1950 (s)	1947 (s)	1956 (s)
				1945 (ms)		



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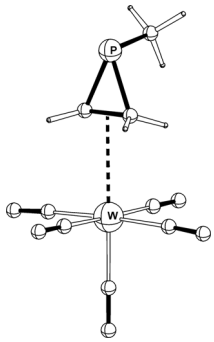

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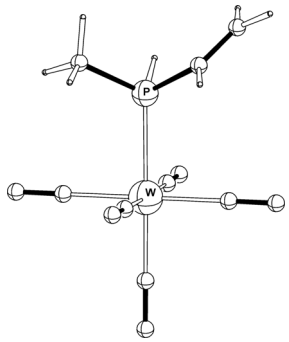

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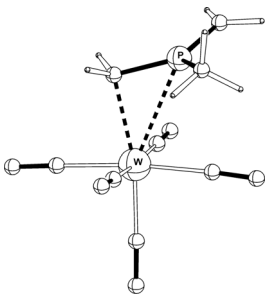

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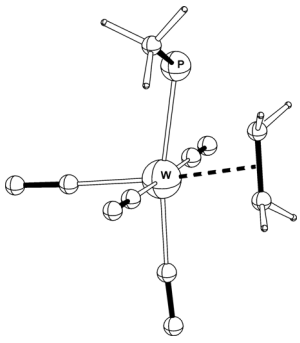
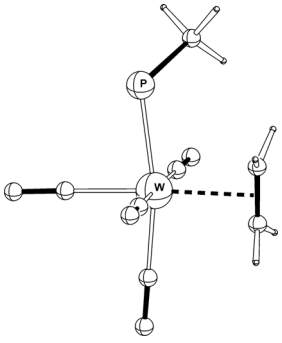


13a



13b

The second fact is that phosphine dissociation definitively took place upon photolysis of **6** in a CO matrix (Scheme 3, path C, X=CO). Cleavage of the P-C bond and consecutive replacement of phosphirane by carbon monoxide results in $W(CO)_6$. A recent computational study on mixed carbonyl-phosphine metal complexes underlined the possibility of photochemical dissociation of both carbonyls and phosphines: the first three excited states for $Cr(CO)_5PR_3$ are repulsive for PR_3 but modestly bonding for its COs.[24] A dynamic analysis showed a small preference for phosphine over carbonyl dissociation.

Moreover, all experimental data of the laser flash photolysis of phosphirane **6** are consistent with phosphine dissociation and the formation of the $W(CO)_5$-moiety interacting with cyclohexane.[25] The observed decay rate is very much similar to reported ones for cyclohexane-$W(CO)_5$ and comparison of the experimental TR-UV/Vis spectra clearly shows that the experimental and the literature spectra match (λ_{max} = 415 nm).[26-27] Recent TRIR data on cyclohexane replacement in cyclohexane-$W(CO)_5$ by THF and substituted THF derivatives also showed, that a pronounced impact of steric factors is to be expected - just as was observed in the experiment.[28] The formation of cyclohexane-$W(CO)_5$ as the transient explains the absence of significant quenching by 1-hexene satisfactorily.

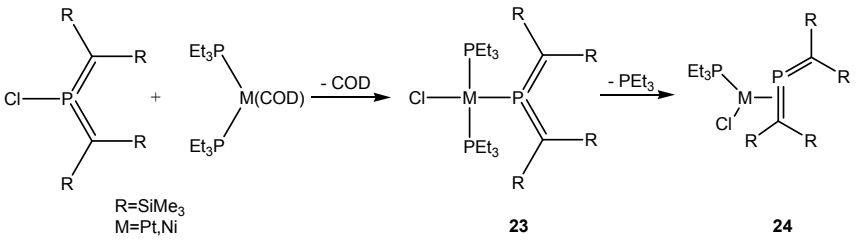
In the matrix, however, phosphine dissociation would lead either to $W(CO)_5Ar$ (**15**), which can be excluded on the basis of previous experimental IR-data[17] (2095, 1963, 1932 cm^{-1}), or to one of several structures where the $W(CO)_5$ moiety interacts with a carbon atom (**17**, **18**) or with a C-C bond (**19**) (Scheme 3). All three are calculated to be more favorable than Ar-complexation (Table 7), but do not yield frequencies in a better agreement with the experiment and can be excluded. The cage-effect is a simple explanation for not observing phosphirane dissociation in noble-gas matrices: if the free phosphirane is hold in proximity to the metal by the matrix atoms the effective quantum yield of photolytic cleavage of the P-W bond will be zero. This is reasonable, given the size of the phosphirane molecule. Consequently, no phosphirane dissociation could be observed.

As was shown in scheme 3 several other reaction paths are possible as well. A number of them can easily be discarded on the basis of the experimental data. For example, no characteristic P-H absorption (~2370 cm^{-1}) was observed in post-photolysis IR spectra, so a 1,2-H shift of phosphinidene **9** to the more stable phosphalkene **10**[4c-d] can be ruled out, as well as the experimentally known[29] rearrangement of phosphirane **6** to vinylphosphine complex (**19**, path F). The formation of a triplet diradical (path E) is highly unlikely as well, because the photoproduct did not react with oxygen and a singlet diradical is expected not to be a minimum on the potential surface.[30]

Other possible reaction pathways cannot be excluded on the basis of the experimental facts alone. Decarbonylation, for example, could be followed by insertion of the uncoordinated $W(CO)_4$-moiety into one of the P-C bonds to form a metallacycle **12**. This structure has been observed in reactions of nucleophilic phosphinidene complexes.[31] Optimization of the metallacycle resulted in a phosphinidene $W(CO)_4$-η^2-olefin complex **13** (scheme 3) of which several conformations can be imagined. All are of significant higher energy than *cis*-**11** (> 16 kcal/mol) and additionally, their CO

frequencies do not correspond with the experimental ones. For example, the two intermediate absorptions calculated for **13a** are more than 65 cm^{-1} higher than those of the photo-product.

The last remaining pathway is rupture of the C-C bond of the phosphirane with the formation of dimethylenephosphorane complex.[32] Interestingly, breaking of this bond and optimization of dimethylenephosphorane structure led to a η^2 2-phospha-allene tungsten complex **22**. An identical experimental η^1-η^2 shift has been reported for platinum and nickel 2-phosphonioallene complexes[33] (scheme 4) and the geometrical parameters of **22** are similar to nickel-complex **24**, e.g. the co-ordinated C-P bond is 1.733 Å (**24**) vs. 1.746 Å (**22**), whereas the uncoordinated C=P is 1.664 vs. 1.666 Å, respectively. The CPC angle (126.9°) is small compared to other bis-methylenephosphoranes (127-136°).[34] Though structure **22** is 7.0 kcal/mol more stable than *cis*-**11**, and could be a viable reaction product, its calculated IR frequencies do not coincide with the experimental ones: several absorptions differ by more than 50 cm^{-1} and an additional, fifth IR-active CO absorption is calculated as well.



Scheme 4 – Rearrangement of a 2-phosponioallene complex.

2.4 Conclusion

After comparison of the number of the experimental CO frequencies and their position in the spectra with those reported for $W(CO)_4ArL$ species and supported by the trend predicted by DFT calculations it is concluded that irradiation of 1-methylphosphirane pentacarbonyltungsten (**6**) with 254 nm in an argon or xenon matrix at 15 K leads to predominant dissociation of an equitorial CO ligand resulting in the formation of *cis*-$W(CO)_4Ar$-phosphirane (*cis*-**11**). In a CO matrix this is suppressed and phosphine dissociation is the major pathway. Photochemical formation of phosphinidene complex **9** is excluded. The dissociation is reversed upon irradiation with $\lambda > 420$ nm. The B3LYP or BP86 functionals in combination with the 6-31G* basis-set and a LANL2DZ basis set for the transition metal do not reproduce the carbonyl IR frequencies accurately enough for these transition metal complexes.

Laser flash photolysis at 266 nm of solutions of phosphirane **6** in cyclohexane cleaves the P-W bond and results in transient $W(CO)_5$(cyclohexane), which is a well-established phenomenon.

2.5 Experimental part

Equipment

The matrix isolation set-up used in this work has been described before.[35] A standard LFP set-up was used. The apparatus consisted of a Spectra-Physics Quanta-Ray Lab 130 Nd-YAG laser operated at 1 Hz repetition rate and 266 nm (50 mJ/pulse, 10ns), a pulsed Xe high-pressure lamp (Müller, Germany) and a Spex Minimate monochromator coupled to a photoelectron multiplier tube. The sample was irraidated at a 90º angle relative to the monitoring beam. To avoid depletion of starting material and product build-up, a flow system was used. Data acquisition was performed using a LeCroy 9361 digital oscilloscope. The entire system was programmed using LabView software. Solutions of **6** were ca. $1.7x10^{-5}$ M in cyclohexane (spectroscopic grade, used as received) for 266-nm excitation. They were purged with argon for 30 min before starting the experiment.

Calculations

All electronic structure and frequency calculations were carried out using the Gaussian 98 suite of programs (G98).[36] The DFT calculations were performed using BP86 exchange-correlation potentials and the 6-31G* basis-set[37] for C, H, O and P, the LANL2DZ basis-set and ECPs[38] for W and the relativistic valence basis-set and relativistic ECPs of Stoll and Preuss (Stuttgart)[18] for Ar and Xe. Minima were confirmed to have only positive force constants. Frequency scaling factors were taken from Scott and Radom.[14]

Synthesis

All experiments were performed under an atmosphere of dry nitrogen. Toluene was distilled from sodium. NMR spectra were recorded on Bruker AC 200 (^{1}H, ^{13}C), Bruker Avance 250 (^{1}H, ^{13}C, ^{31}P) spectrometers, IR spectra on a Mattson-6030 Galaxy FT-IR spectrophotometer, and high-resolution mass spectra (HRMS) on a Finnigan MAT 900 spectrometer. NMR-chemical shifts are internally referenced to the solvent for ^{1}H ($CDCl_3$: 7.25 ppm, C_6D_6: 7.15 ppm) and ^{13}C ($CDCl_3$: 77.0 ppm, C_6D_6: 128 ppm) and externally for ^{31}P to 85% H_3PO_4. [7-Me- and [7-phenyl-5,6-Methyl-2,3-bis(methoxycarbonyl)-7-phosphanorbornadiene] pentacarbonyl tungsten **1**,[6, 39] and 1-methyl-2,3-diethyl-1*H*-phosphirene pentacarbonyltungsten **7**[6a] were synthesized according to literature methods. Ethylene was purchased from Hoek Loos. CuCl was purchased from Aldrich and used as such.

*1-Methylphosphirane pentacarbonyltungsten (**6**):* 100 mg (0.17 mmol) of complex Me-**1** was dissolved in 2 ml toluene and transferred to a 5 ml pressure chamber. A suspension of a little CuCl in 1 ml toluene was added and the channel was rinsed with 1 ml toluene. 65 bar ethylene pressure was applied and the solution was stirred for a night at 40ºC, after which the yellow color had paled. The solution was removed from the chamber, the solvent was evaporated and the light brown residu was purified by chromatography and sublimation. White powder, 50 mg (0.13 mmol, 74%). ^{31}P NMR ($CDCl_3$): δ -199.3 ($^1J_{PW}$=254.1 Hz). ^{13}C NMR ($CDCl_3$): δ 196.0 (d, $^2J_{CP}$=8.4 Hz, CO_{eq}), 17.3 (d, $^1J_{CP}$=15.8 Hz, CH_3), 9.1 (d, $^1J_{CP}$=10.8 Hz, CH). ^{1}H NMR ($CDCl_3$): δ 1.38 (d, $^2J_{HP}$ = 7.5 Hz, 3H, CH_3), 1.09-1.35 (m, 4H, CH_2). IR (KBr): ν (cm^{-1}) 2074.3 (m), 1929.7 (s), 1101.3 (w), 1023.2 (w), 948.0 (w), 597.9 (w), 572.8 (w). HRMS: Calculated for $C_8H_7PO_5W$: 397.95410, found: 397.95462. M/*z* (%): 398 (45, $[M]^+$), 370 (8, $[M\text{-}CO]^+$), 286 (100, $[M\text{-}4CO]^+$), 256 (76, $[M\text{-}5CO]^+$), 228 (56, $[M\text{-}5CO\text{-}C_2H_4]^+$), 43 (86, $[C_3H_7]^+$).

Acknowledgements

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Supporting Information

Supporting information containing the calculated energies and *xyz*-coordinates of the species discussed is available from the author.

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Chapter 3

Infrared-, UV/Vis-, and W-band ESR-Spectroscopic Characterization and Photochemistry of Triplet Mesitylphosphinidene

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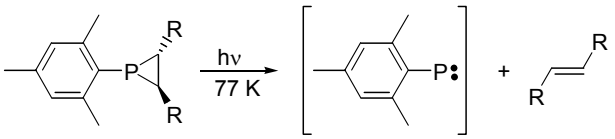
3.1 Introduction

Whereas many simple carbenes [R_2C][1] and nitrenes [RN][2-4] have been detected by various spectroscopic techniques, this is not the case for analogous phosphinidenes [RP].[5-7] In sharp contrast to the abundant evidence of transition-metal complexed phosphinidenes,[8-10] evidence of noncomplexed phosphinidenes has remained elusive except for a recent matrix-IR study by Glatthaar and Maier[11] on H_3SiP, generated by the reaction of atomic silicon with phosphine, and an earlier electron paramagnetic resonsance (EPR) study by Gaspar and co-workers[12] on mesitylphosphinidene (2,4,6-$Me_3C_6H_2P$; MesP; **3**), which was obtained by photolysis of *trans*-1-mesityl-2,3-dimethyl-phosphirane (**1**) in methylcyclohexane at T = 77 K (Scheme 1). No other direct experimental confirmation has been obtained for MesP.



1 R = Me
2 R = H

3

Scheme 1 - Photochemical formation of triplet MesP.

Theoretical studies concur with the spectroscopic observation that a strongly preferred triplet ground state is predicted for the arylphosphinidene.[13-14] From the X-band EPR spectrum, a zero field splitting (ZFS) parameter D, of $|D/hc| = 3.521$ cm^{-1}, was determined,[12] which is much larger than that for triplet phenylnitrenes (~ 1 cm^{-1}) and triplet phenylcarbenes (~ 0.5 cm^{-1}). The unusually large D value was attributed to second-order spin-orbit contributions. Recent calculations on spin-orbit coupling in alkyl nitrenes, phosphinidenes, and arsinidenes yielded a D value of $|D/hc| = 3.46$ cm^{-1} for triplet methyl phosphinidene,[15] in line with the results of Gaspar *et al.*[12] However, it should also be noted that on photolysis of more congested phosphiranes Yoshifuji and co-workers[16] were unable to obtain an EPR signal in the reported region other than a weak signal at 5K that was believed to be due to triplet oxygen.

We have investigated the photochemistry of **1** and **2**, using the tools of matrix isolation spectroscopy and laser flash photolysis; herein we report EPR, infrared, and UV/Vis data that unequivocally support the formation of mesitylphosphinidene **3**.

3.2 Results and Discussion

Initially, using an X-band ESR spectrometer, we tried in vain to reproduce the EPR spectrum reported by Gaspar and co-workers.[12] Photolysis (248 nm, KrF-excimer, or 254 nm) of **2**, matrix-isolated in glassy methylcyclohexane ($T = 5$ K), resulted in the formation of yellow matrices, but the spectra only showed strong doublet signals around $g = 2$ (g is the g facrot) without EPR transitions attributable to triplet **3**. However, employing a W-band (95 GHz) EPR spectrometer, a very weak signal was detected exactly at the place predicted (4926 mT, Figure 1) for a triplet species with the ZFS parameters reported by Gaspar and co-workers; a background scan without sample showed no transitions in this spectral regime.

Monitoring by IR spectroscopy of the photolysis ($\lambda_{exc} = 254$ nm, 48 h) of **1** or **2**, matrix-isolated in Ar at 10 K, showed slow disappearance of its IR bands and formation of very weak new bands. Some of these are attributable to *trans*-2-butene (from **1**) or ethylene (from **2**), respectively, whose IR spectra were also recorded independently by matrix isolation of authentic material. The remaining bands are assigned to triplet mesitylphosphinidene **3** based on the comparison with the calculated IR spectrum at B3LYP/6-31G(d) (Table 1).

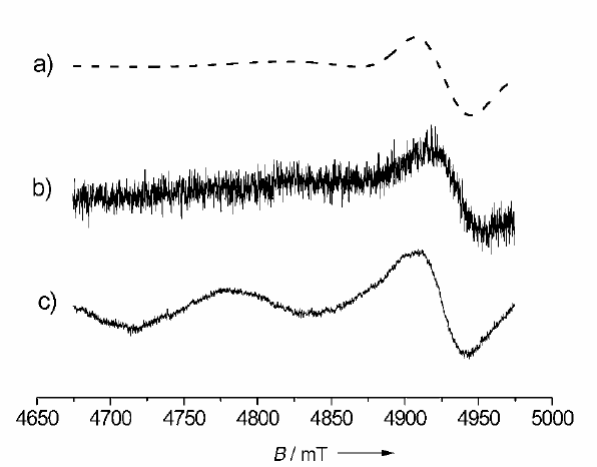


Figure 1 - W-band ESR spectra of a sample of 2 in polycrystalline cyclohexane (T = 5 K), irradiated for 60 min with λ = 254 nm. a) Simulated spectrum. Simulation parameters: line width = 10 mT, D = - 3770.6 mT ($|D/hc|$ = 3.521 cm^{-1}). b) Experimental spectrum obtained by sweeping the magnetic field from lower to higher values and c) from higher to lower values.

When the sample was subjected to further irradiation (λ_{exc} = 385 – 420 nm or λ_{exc} > 455 nm, 90 min), the IR bands belonging to both triplet **3** and *trans*-2-butene or ethylene disappeared, while those of the starting materials **1** or **2** partially re-emerged, together with a new set of IR bands.[18a] This new photoproduct showed a broad IR band at $\tilde{\nu}$ = 2261.2 cm^{-1}, indicating the presence of a P-H bond. By comparison with a calculated IR spectrum (B3LYP/6-31G(d)), it could be identified as 1*H*,2*H*-dihydrobenzophosphete **4** (Figure 2, Table 2).[18b] Intramolecular C-H insertion of the phosphorus center of supermesitylphosphinidene (Mes*P) into the ortho-tBu group to give a phosphaindane is common[6-7] and λ^5-benzophosphetes have been reported previously.[19] The new dihydro-λ^3-benzophosphete **4**, which is energetically favored over triplet **3**, may be formed similarly or via phosphaquinone methide **5** (Scheme 2).

The UV/Vis spectrum further supports the photochemical formation of **3** from matrix-isolated phosphiranes **1** (and **2**). Photolysis (λ_{exc} = 254 nm, 80 min, Ar, 10 K) gave rise to two new strong absorptions at λ = 278 and 292 nm, three weaker ones around 350, 370, and 390 nm, and a weak, broad one with fine structure between 420 and 470 nm. Subsequent long-wavelength photolysis (λ_{exc} > 455 nm) resulted in depletion of the absorptions at λ = 278, 292, 350, and > 420 nm, while those at λ = 370 and 390 nm initially increased in intensity (Figure 3). Extended near-UV photolysis (λ_{exc} = 360 – 400 nm, 2h) resulted in bleaching of all absorptions with λ > 300 nm.

Table 1 - Calculated and experimental IR data of **3** (range 1700 to 500 cm^{-1})

No.	$\tilde{\nu}$ (calc.) [cm^{-1}]	$\tilde{\nu}$ (calc.) (* 0.97)	calc. intensity [km mol^{-1}]	$\tilde{\nu}$ (exp.) [cm^{-1}]	exp. intensity	description[a]
44	1527.6	1481.8	8.3	-	-	δ_{as} *o*-CH_3
43	1523.0	1477.3	33.0	1456.9	s	δ_{as} *o*-CH_3
42	1516.5	1471.0	5.6	-	-	δ_{as} *p*-CH_3
41	1515.9	1470.4	9.3	-	-	δ_{as} *p*-CH_3
40	1512.6	1467.2	0.2	-	-	τ *o*-CH_3
39	1511.5	1466.2	15.9	1431.1	w	τ *o*-CH_3
38	1457.6	1413.9	1.6	1407.3	vw	19B + τ *p*-CH_3
37	1445.8	1402.4	3.1	1398.9	w	δ_s CH_3
36	1443.3	1400.0	1.4	1377.0	m	δ_s CH_3
35	1443.3	1400.0	1.0	-	-	19A + δ_s CH_3
34	1439.2	1396.0	1.2	-	-	δ_s CH_3
33	1319.2	1279.6	1.6	1296.0	vw	14
32	1309.9	1270.6	9.4	1286.2	w	13
31	1271.5	1233.4	0.8	1237.8	vw	3
30	1206.5	1170.3	0.3	1170.5	vw	9A
29	1074.9	1042.7	2.2	-	-	17B + ρ CH_3
28	1070.8	1038.7	0.0	-	-	17A + ρ CH_3
27	1068.3	1036.3	5.0	1033.3	w	ρ CH_3
26	1065.3	1033.3	19.2	1028.9	m	ρ CH_3
25	1059.7	1027.9	0.7	-	-	ρ CH_3
24	1041.9	1010.6	0.0	-	-	ρ CH_3
23	1026.8	996.0	1.9	993.0	vw	ρ CH_3
22	973.9	944.7	1.1	-	-	ρ CH_3
21	941.1	912.9	0.3	-	-	ρ CH_3
20	898.0	871.1	0.0	-	-	10A
19	874.0	847.8	12.5	849.8	m	5
18	725.5	703.7	0.9	709.7	w	4
17	630.5	611.6	4.8	625.8	w	6A
16	572.8	555.6	0.03	542.9	vw	12

[a] Descriptions analogous to those of the vibrations of benzene as proposed by Pitzer and Scott.[17]

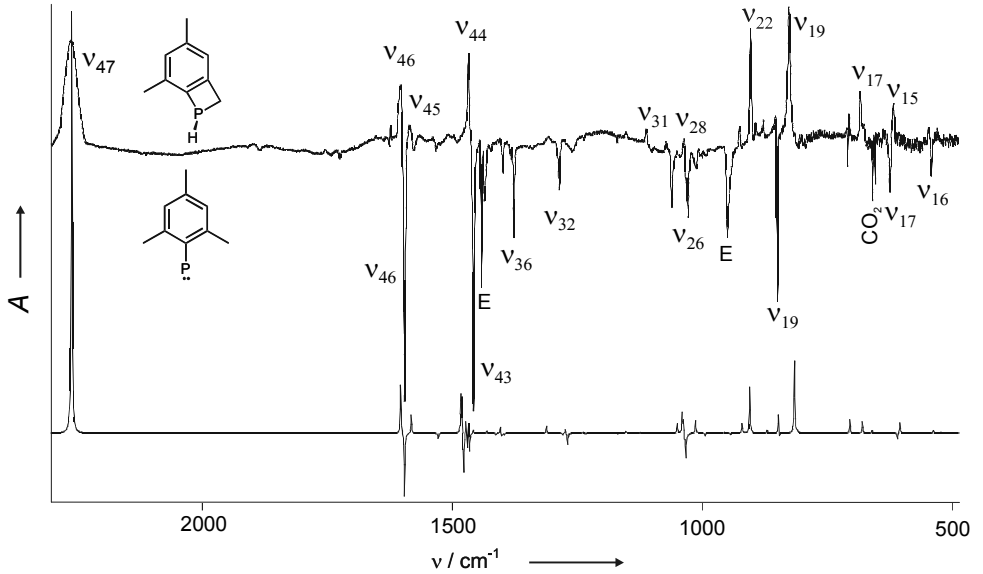


Figure 2 - *Top spectrum*: Difference IR spectrum (Ar, 10 K) of the spectra obtained after photolysis of **2** at λ_{exc} = 254 nm (48 h) and subsequently at λ_{exc} > 385 nm (90 min). Bands pointing down disappear on photolysis at λ_{exc} > 385 nm and are attributed to a mixture of ethylene (E) and triplet **3**. The splitting of phosphinidene bands at $\tilde{\nu}$ = 1028.6 and 1061.3 cm^{-1} (ν_{26}) is likely due to Fermi resonance.[18b] Several very weak bands remain unassigned. Bands pointing up are attributed to the secondary photoproduct **4** and traces of **2**. The highest intensity of the difference spectrum amounts to ca. 0.1. The assignment of a number of selected bands has been indicated by giving the transition numbers (c.f. Tables 1 and S1). *Bottom spectrum*: calculated IR difference spectrum (0.97 x scaling, (U)B3LYP / 6-31G(d)) of **4** minus triplet **3**.

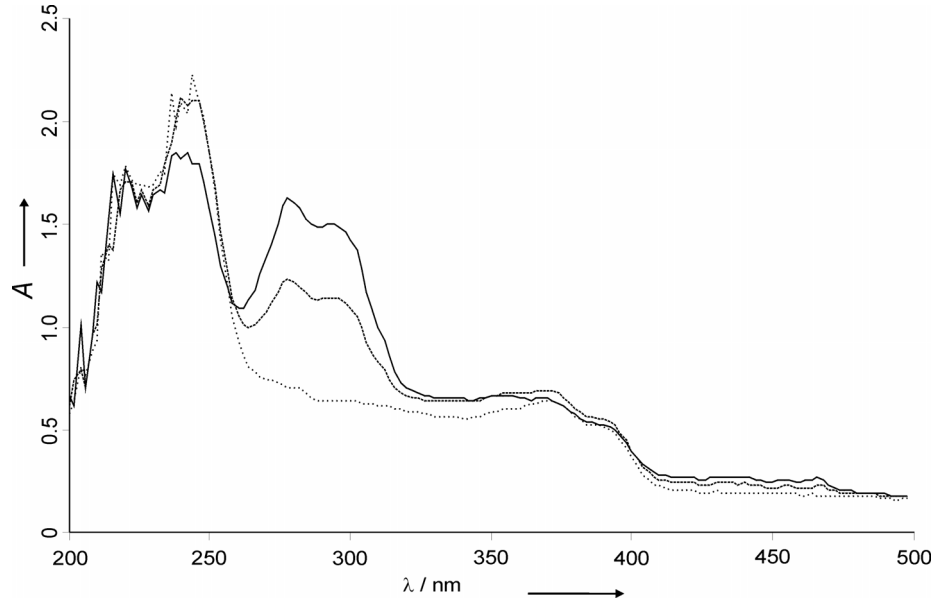
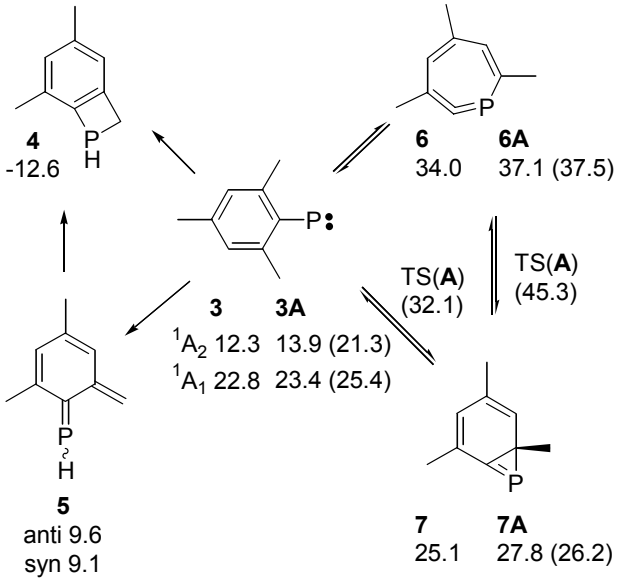


Figure 3 – UV/Vis spectra (Ar, 10 K) obtained after photolysis of 1. *Solid line*: after photolysis at λ_{exc} = 254 nm for 80 min. *Dashed line*: after subsequent photolysis at λ_{exc} > 455 nm for 10 min. *Dotted line*: after extended photolysis at λ_{exc} > 455 nm for 100 min.



Scheme 2 - B3LYP/6-31G(d) energies (in kcal/mol) for the $C_9H_{11}P$ and unsubstituted C_6H_5P (**A**) isomers relative to triplet **3** and **3A**. CASPT2(8/8)/6-31G(d) energies for **A** are given in parentheses.

These observations are rationalized by assigning the absorptions λ = 278, 292, 350, and 420-470 nm to triplet mesitylphosphinidene **3**, and those at λ= 370 and 390 nm to a secondary photoproduct other than **4**. The UV/Vis spectrum of **3**, with the weak, structured broad band extending to λ = 470 nm, strongly resembles the UV/Vis spectra of known triplet arylnitrenes.[4a] The intense excitations at λ = 285, 310, 340, 415 and 440 nm calculated with time-dependent B3LYP/6-311+G(d,p)[20] for triplet mesitylphosphinidene provide convincing evidence that triplet 3 is indeed formed upon photolysis of matrix-isolated mesitylphosphiranes **1** and **2**,[21] albeit in small yield.[22] The origin of the 370 and 390 nm absorptions cannot be attributed to secondary photoproduct **4**, because its calculated UV/Vis spectrum (TD-B3LYP/6-311+G(d,p)) gives a longest-wavelength absorption at λ_{max} = 255 nm. Among the compounds considered, the calculated spectrum of didehydrophosphepine **6** (λ_{max} = 360 and 385 nm) matches best with the experimental data.[23-24] Formation of **6** from **3** may occur by ring-enlargement, either directly[25] or via bicyclic phosphirene **7**.[26] Borden and co-workers[27] showed with CASPT2 that the ring expansion of singlet phenylphosphinidene **3A** to **6A** (via **7A**) is endothermic with sizeable barriers (Scheme 2); our B3LYP/6-31G(d) calculations give similar results except for the state $^1A_2$ of the parent molecule.[28] The tentative assignment of didehydrophosphepine **6** as a minor photoproduct may appear surprising as it is the least stable isomer of those considered, though bulky linear phospha-allenes are known.[29] However, steady-state irradiation under conditions of matrix isolation spectroscopy frequently allows for the observation of processes that are thermodynamically unfavorable and whose outcome mostly depends on the concentration of photostationary equilibriums.

Finally, we explored laser flash photolysis (LFP) of an argon-purged cyclohexane solution of **1** at ambient temperature with a 266 nm excitation and nanosecond time resolution. The resulting transient spectrum (Figure 4) contained a single species with λ_{max} = 285 nm (vs) and 400 – 475 nm (broad, weak) and a lifetime τ = 13 µs, which we assign to phosphinidene **3** based on the similarity with the UV/Vis spectrum of the matrix-isolated species at 10 K (Figure 3). The transient could be quenched with oxygen,[30] and reacted with the π-systems ethyl propiolate HC≡CCOOEt (k_{ETP} = (7.7 ± 1.1) · 10^6 l mol^{-1} s^{-1}) and tetramethylallene (k_{TMA} = (5.0 ± 0.8) · 10^6 l mol^{-1} s^{-1}, see Figure 5), but not with 1-hexene. This profile supports triplet **3**, which is expected to give an allylic triplet diradical with tetramethylallene, while such stabilization cannot occur with hexene as reaction partner.

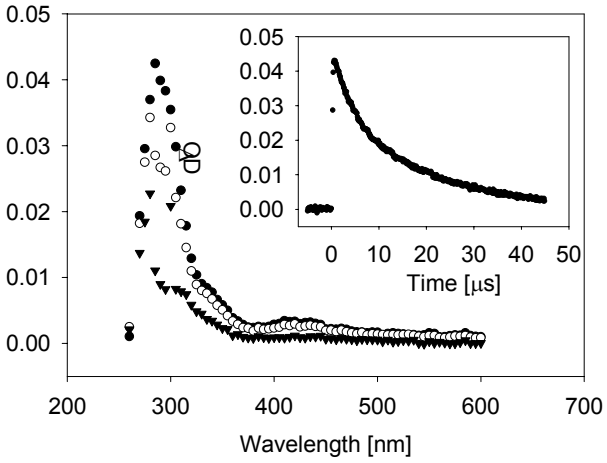


Figure 4 - Transient spectra, recorded after LFP (λ_{exc} = 266 nm) of phosphirane **1** in cyclohexane under Ar atmosphere. Black circles: 470 ns after LFP, white circles: 1.7 µs after LFP, black triangles: 75 µs after LFP.
Inset: transient trace, monitored at λ = 285 nm.

3.3 Conclusion

In conclusion, we have unequivocally identified triplet mesitylphosphinidene **3** as primary reaction product in the photolytic cleavage of phosphiranes **1** and **2**, using a variety of low-temperature and time-resolved spectroscopic techniques. Under conditions of matrix isolation, **3** is formed in very low yield only, which is likely due to efficient photoinduced addition of **3** to the alkene still present in the matrix cage. Upon further irradiation, **3** rearranges to 1*H*,2*H*-dihydrobenzophosphete **4**. Results obtained using laser flash photolysis provide further support for the formation of **3**, and show that **3** will readily be quenched by reactive π-systems. Further studies on the photochemistry of **1**, **2**, and related compounds are in progress.

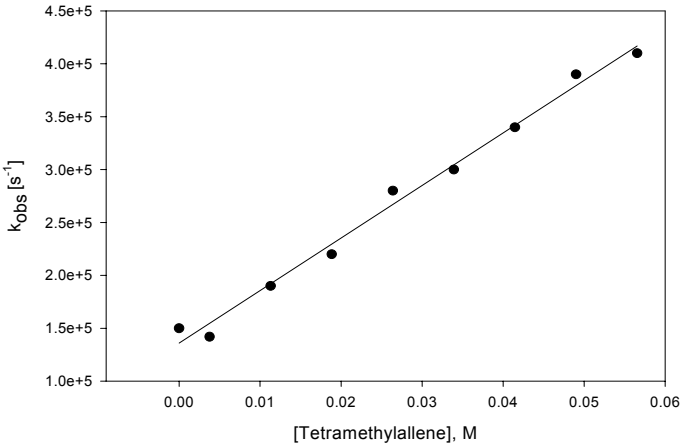


Figure 5 - Laser flash photolysis (λ_{exc} = 266 nm) of **1**. Plot of the rate constant of decay, measured at λ = 285 nm, vs. the concentration of tetramethylallene. The straight line gives a linear fit of the experimental data. (r^2 = 0.9899).

3.4 Experimental part

The matrix isolation set-up used in this work has been described before.[31] As light sources, a Hg low pressure lamp (λ = 254 nm; Gräntzel, Germany) and Hg high pressure lamps (Osram, 500 W, Oriel housing, in combination with cut-off filters) were used. Argon (Messer-Griesheim, 99.999%) was used as matrix material. Compounds **1** and **2** were synthesized according to literature procedures.[32] Deposition was performed using the slow spray-on technique at a sample temperature of 20 °C. *Trans*-2-butene (99%) was obtained from Matheson and deposited as 0.1% / 99.9% mixture with Ar. X-band ESR-spectroscopic measurements were performed using a Bruker Elexsys E500 ESR spectrometer with an ER077R magnet (75 mm pole cap distance) and an ER047 XG-T microwave bridge. Frozen solutions of **2** in methylcyclohexane were irradiated both within the resonator cavity (T = 5 K) using a Lambda-Physik Compex 110 excimer laser operated with Kr/F_2 (248 nm, 200 mJ / pulse) or externally (T = 77 K), using λ = 254 nm (Hg low-pressure lamp). W-band ESR-spectroscopic measurements employed a Bruker Elexsys E680 spectrometer. Prior to measurement, a degassed solution of **2** in cyclohexane was irradiated (λ = 254 nm, 60 min, T = 77 K) in a quartz capillary cooled to 77 K in a quartz dewar and transferred frozen into the precooled cryostat. Experimental parameters: frequency = 94.185061 GHz, microwave power = 15 dB, modulation amplitude = 0.1 mT, modulation frequency = 100 kHz. Simulations were performed using the Easyspin routine[33] and all the parameters entering the simulation are given in the figure caption.

The set-up used for laser flash photolysis has been described before.[34] Solutions (ca. 0.1 mM) of **1** in cyclohexane (Baker, spectroscopic grade) were purged with Ar for 20 min. prior to the experiment. Tetramethylallene (Aldrich) and ethyl propiolate (Fluka) were of the highest purity commercially available. They were used as received. 1-Hexene (Aldrich) was freshly distilled immediately prior to the experiment.

All calculations were performed with the Gaussian 98 suite of programs.[35] All geometry optimizations and frequency calculations (scaled by 0.97)[36] were performed at (U)B3LYP/6-31G(d). UV spectra were calculated using TD DFT (B3LYP/6-311+G(d,p)).

Table 2 - Calculated and experimental IR data of **4** (range 2400 to 500 cm^{-1}).

No.	$\tilde{\nu}$ (calc.) [cm^{-1}]	$\tilde{\nu}$ (calc.) (* 0.97)	calc. intensity [km mol^{-1}]	$\tilde{\nu}$ (exp.) [cm^{-1}]	exp. intensity	description[a]
47	2330.9	2261.1	151.3	2261.2	vs	ν P-H
46	1652.6	1603.0	17.7	1602.3	m	8A
45	1631.8	1582.8	6.8	1585.3	w	8B
44	1529.0	1483.1	12.2	1467.5	m	δ_{as} 2-CH_3
43	1527.3	1481.5	15.3	-	-	δ_{as} 4-CH_3
42	1518.2	1472.7	5.7	-	-	δ_{as} 2-CH_3
41	1513.9	1468.5	6.1	-	-	δ_{as} 4-CH_3
40	1503.5	1458.4	1.3	-	-	δ CH_2
39	1476.2	1431.9	1.0	-	-	19A + δ CH_2
38	1447.7	1404.3	2.4	-	-	19B + δ_{as} CH_3
37	1443.0	1399.7	0.5	-	-	δ_s CH_3
36	1440.7	1397.5	0.1	-	-	δ_s CH_3
35	1353.2	1312.6	2.3	1307.5	vw	14
34	1314.8	1275.4	1.6	-	-	13
33	1278.0	1239.7	0.5	-	-	3
32	1189.3	1153.6	0.8	1152.7	vw	9A
31	1160.0	1125.2	0.3	1113.2	w	ω CH_2
30	1101.8	1068.7	0.2	1073.2	vw	τ CH_2
29	1083.5	1051.0	3.4	1051.6	vw	ρ CH_3
28	1073.4	1041.2	7.9	1037.0	w	ρ CH_3 +17B
27	1071.0	1038.9	5.0	-	-	ρ CH_3 + 17B
26	1045.9	1014.5	4.7	-	-	ρ CH_3
25	1040.4	1009.2	0.3	-	-	ρ CH_3
24	987.6	958.0	0.3	-	-	ρ CH_3
23	950.3	921.8	3.3	926.0	w	ρ CH_3+ CH_2 + δ PH
22	935.0	907.0	16.7	901.1	s	ρ CH_2 + δ P-H
21	898.3	871.4	1.3	878.4	vw	10A
20	874.7	848.5	9.4	854.3	w	5
19	842.0	816.7	25.8	827.5	s	δ P-H
18	728.7	706.8	4.9	708.1	w	ρ CH_2 + δ P-H
17	702.5	681.4	4.1	685.3	m	ρ CH_2 + δ P-H + 4
16	683.4	662.9	1.2	-	-	ν P-CH_2
15	625.2	606.4	3.9	618.5	w	6A
14	579.6	562.2	0.1	-	-	12
13	555.9	539.2	1.4	549.8	vw	6B
12	542.2	525.9	0.3	531.8	vw	16B + ρ CH_3

[a] Description analogous to those of the vibrations in benzene as proposed by Pitzer and Scott.[17]

Acknowledgements

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Supporting information

Supporting Information for this article with the energies, frequencies, excited states and *xyz* co-ordinates of the calculated species is available on the WWW under http://www.angewandte.org or from the author (M.B.)

3.5 Notes and References

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[18] a) The ratio between **1** (**2**) and **4** that results on photolysis of **3** in the presence of the alkene in the matrix cage decreases with longer irradiation times. b) The observed spectrum of **3** has two medium intensity bands at ν˜ = 1040 – 1070 cm^{-1}, but only one is calculated. This may be due to Fermi resonance between the bands at ν˜ (calc.) = 1065.3 cm^{-1} (A') and ν˜ (calc.) = 572.8 cm^{-1} (A', exp. 542.9 cm^{-1}), which would split the one at 1065.3 cm^{-1} (calc.) into the two components observed at 1028.6 and 1061.3 cm^{-1}.

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[22] The reversibility of the phosphirane cleavage indicates that the low yield of **3** is due to an unfavorable photostationary equilibrium rather than either a very low quantum yield or pronounced filter effects.

[23] The observation of an extremely weak IR band at $\tilde{\nu}$ = 1723.7 cm^{-1} supports the formation of **6** (C=C=P stretching mode: calc. 1712.9 cm^{-1} (scaled by 0.97), weak).

[24] Phosphaquinone methide **5** (*anti*-**5**: calc. λ_{max} = 482 nm; *syn*-**5**: calc. λ_{max} = 495 nm) and bicyclic phosphirene **7** (calc. λ_{max} = 334 and 494 nm) are less likely candidates.

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Chapter 4

Novel Strained, Stable 2-Aza-1-Phosphabicyclo-[*n*.1.0]alkane and –alkene $Fe(CO)_4$ Complexes with Dynamic Phosphinidene Behavior

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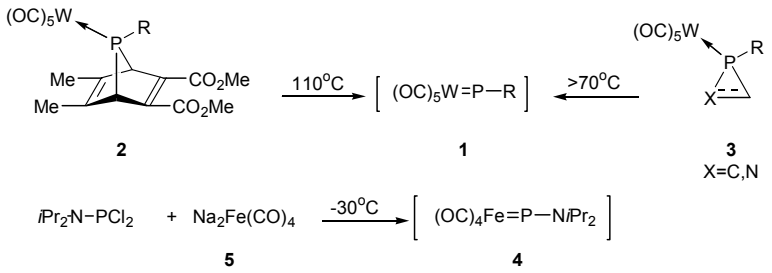
4.1. Introduction

Phosphinidenes, [R-P], the phosphorus analogues of carbenes,[1] are elusive species,[2] yet when coordinated to a transition metal group, [R-P=ML_n], they are remarkably versatile with a significant synthetic scope.[3] There are two types, transient electrophilic or Fischer-type terminal phosphinidene complexes and those that are much more stable and nucleophilic or Schrock-type.[4] The electrophilic ones, particularly [R-P=$W(CO)_5$] (**1**), give access to many different heterocycles via addition to unsaturated bonds.[3] Cheletropic elimination from complexed 7-phosphanorbornadienes (**2**) is the most popular route to **1**,[5] but retroaddition from phosphiranes[6] or azaphosphirenes[7] (**3**) is also used occasionally. Both routes are hampered by the tedious synthesis of the precursors. A much more convenient ionic path was recently reported by us for transient [*i*Pr_2N-P=$Fe(CO)_4$] (**4**) that simply

involves reacting Collman's reagent (**5**) with a dichlorophosphane.[8] It was shown that this reagent is electrophilic as it adds to olefins and alkynes, but also that it appears less reactive than **1**, because the formed phosphiranes are thermally labile and easily give retroaddition.[9]



Scheme 1 – Several methods of phosphinidene generation.

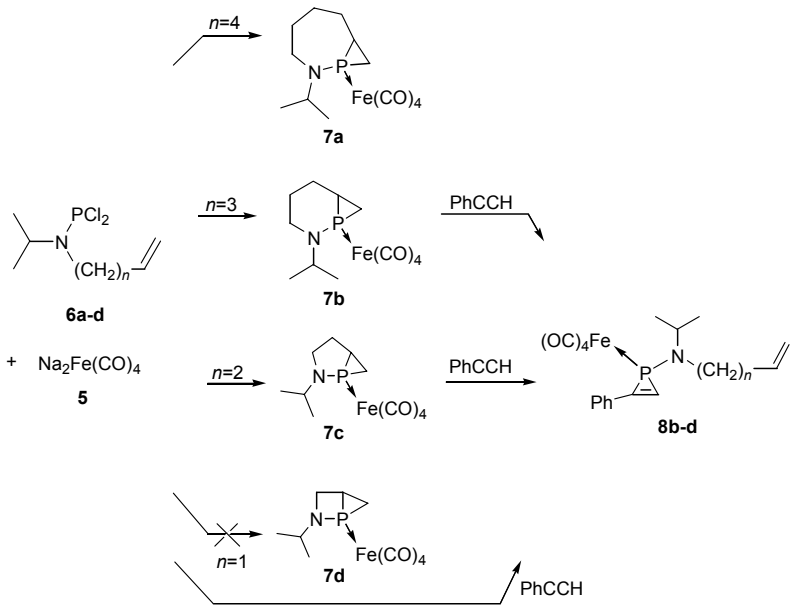
In the present paper we expand on this ionic path and will show that stable bicyclic phosphiranes and phosphirenes can be formed by intramolecular cycloaddition of [R-P=Fe(CO)$_4$] to respectively the double or triple bond containing substituent R. Despite their stability, these bicyclic phosphorus heterocycles can undergo retroaddition, which will be illustrated by an intramolecular transfer of the carbene-like phosphinidene group.

4.2 Results and Discussion

In the first part the formation and properties are described of differently sized bicyclic phosphiranes resulting from the reaction of Collman's reagent with various dichloro aminophosphines of which the amino group carries a terminal olefinic group. As a special component a stable, but dynamic system will be presented in which the phosphinidene group transfers intramolecularly between olefinic groups. In the second part we address the intramolecular phosphinidene cycloaddition to triple bonds, instead of double bonds, to form the more strained unsaturated bicyclic products. The synthesis of all starting materials is described in the Experimental Part.

4.2.1 Bicyclic phosphiranes

Reaction of $Na_2Fe(CO)_4 \cdot 1.5$ dioxane (Collman's reagent) with dichloro(dialkylamino)phosphines in diethyl ether or tetrahydrofuran at –30°C results in the formation of various types of Fe/P-clusters depending on the alkyl substituent and the reaction conditions.[10] Intermediate transient phosphinidene complex [*i*Pr$_2$N-P=Fe(CO)$_4$] (**4**) is trappable, both as a phosphirane[8a] and a phosphirene,[8b] showing that its affinity for terminal olefins and alkynes exceeds the self condensation process. To examine the scope of this process we introduced additional ring strain by reacting the transient phosphinidene iron complex intramolecularly with an olefinic group present in the amino substituent. Four cases are considered in which the length *n* of the alkyl chain $(CH_2)_n$ that separates the olefin group from the amino nitrogen varies from 1 to 4. We start with the longest chain ($n = 4$), as it presumably efforts the least strain on cyclization (Scheme 2).



Scheme 2 - Synthesis and reactivity of bicyclic phosphiranes **7**.

Reaction of **6a** with Collman's reagent in diethyl ether at –30°C resulted after flash chromatography (–15°C) in an orange oil (53%) that consisted mainly (95%) of the desired 2-aza-1-phosphabicyclo[5.1.0]octane **7a** besides P,P-coupling products. The bicyclic structure is supported by a ^{31}P NMR resonance at –41.3 ppm that is typical for a $Fe(CO)_4$ complexed phosphirane,[8a] and by the different ^{1}H NMR resonances for the geminal methylene hydrogens of the 3- and 7-membered rings. The conformational flexibility of **7a**, which likely occurs through inversion at the nitrogen center, is illustrated by the splitting of its ^{31}P NMR resonance at –41.3 ppm into two of nearly equal intensity at –34.5 and –47.8 ppm at –78°C. B3LYP/6-311+G(d,p) calculations[11] on model structures (labeled with capital letters, without $Fe(CO)_4$ and having a Me instead of a *i*Pr substituent) support the existence of different diastereomers. A difference of 15.5 ppm in ^{31}P NMR chemical shifts is calculated for the lowest two energy structures of **7A** (Figure 1) that have a chair-boat conformation with the amino substituent in either an equatorial or axial position.

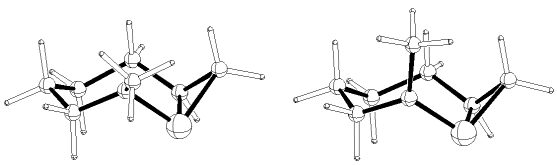


Figure 1 - B3LYP/6-311+G(d,p) diastereomers and energies (in kcal/mol) of **7A** with equatorial (I) and axial (II) N-Me groups.

The balance between **7a** and the P,P-coupling products illustrates a marginal preference for cycloaddition of the transient phosphinidene iron complex to the olefinic group over its self condensation. The limited stability of **7a** hampered further purification, but suggests that strain in the bicyclic structure may indeed be a limiting factor.

Reaction of Collman's reagent with **6b**, which has a shorter alkyl chain (n = 3) for the olefinic substituent, surprisingly gives the tighter 2-aza-1-phosphabicyclo[4.1.0]heptane **7b** in a remarkably good isolated yield (63%) as a stable yellow solid (m.p. 60-62°C). X-ray single crystal structure determination[12] confirmed the bicyclic structure of **7b** (Figure 2) and showed it to be in an axial position to the Fe-complex, as expected for a weak π-acceptor ligand.[13] We are aware of only one other somewhat related crystal structure, namely that of the monocyclic 2,3,3-tri(trimethylsilyl)-phosphirane $Fe(CO)_2Cp$-complex.[14] The structural data of the C_2P ring of **7b** compare well with those of $W(CO)_5$-complexed phosphiranes.[15] For example, the P-C bond distances of 1.8053(18) and 1.8115(19) Å are in the normal range (1.78–1.89 Å) just like the 50.52(9)° CPC angle (c.f. 47.4–51.1°). Also the six-membered heterocyclic ring with its half-chair conformation appears to have normal P-N, C-N, and C-C bonds. Both the *i*Pr substituent and the metal-fragment are oriented in the equatorial position. In solution, the observed ^{31}P NMR chemical shift at –45.2 ppm is very similar to that found for **7a**, but the more condensed structure of **7b** is evident from its more shielded ^{13}C NMR chemical shifts with differences of 6 and 8 ppm for those of the phosphirane ring. Also the ^{1}H NMR chemical shifts particularly of the *endo* and *exo* methylene hydrogens of this ring are more shielded (0.87 and 1.47 ppm) with a larger difference between them (**7b** $\Delta\delta_H$ 0.61, **7a** $\Delta\delta_H$ 0.39). The nearly exclusive formation of **7b** might suggest the bicyclic structure to be less strained than that of **7a**, which may be due to the preference of the phosphorus atom for tighter bond angles.

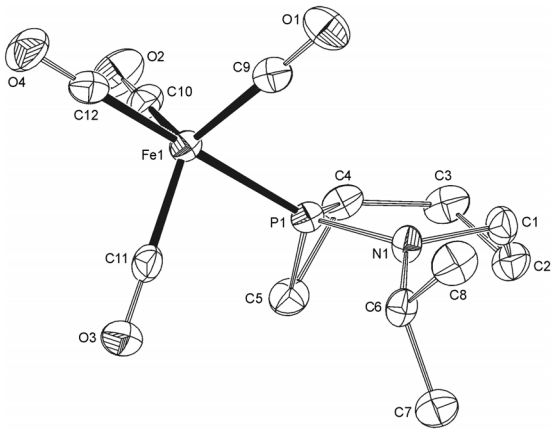
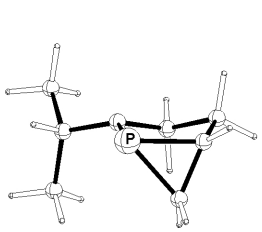
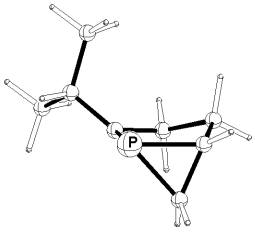


Figure 2 - Displacement ellipsoid plot (50% probability level) of **7b**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (deg) and torsion angles (deg): P1-Fe1 2.2222(5), P1-N1 1.6554(15), P1-C4 1.8053(18), P1-C5 1.8115(19), C4-C5 1.543(3), Fe1-C9 1.801(2), P1-C4-C5 64.95(10), P1-C5-C4 64.53(10), P1-Fe1-C9 88.15(6), Fe1-P1-N1 120.24(5), N1-P1-C4 106.06(8), N1-P1-C5 111.64(9), C4-P1-C5 50.52(9), C9-Fe1-P1-C5 -170.61(10), Fe1-P1-N1-C6 57.77(14), N1-P1-C4-C3 -6.26(18)

The still more condensed bicyclic structure, 2-aza-1-phosphabicyclo[3.1.0]hexane **7c**, was obtained as a yellow liquid in 64% isolated yield from reaction of Collman's reagent with **6c** in which the double bond is separated from the nitrogen by a C_2H_4 unit. Its ^{31}P NMR chemical shift at –19 ppm is deshielded by more than 20 ppm from those of the larger bicyclic structures (**7a**, **b**) and reported iron complexed amino phosphiranes.[8a,9] The ^{13}C NMR chemical shifts of the carbons of the phosphirane ring are shielded compared to those of **7b** ($\Delta\delta_C$ 7.7 and 2.8), as are its geminal methylene hydrogens ($\Delta\delta_H$ 0.33 and ~0.7) with still larger difference between them (**7c** $\Delta\delta_H$ ~0.96, **7b** $\Delta\delta_H$ 0.61). The $\Delta\delta_H$ of 0.96 for the (*exo-endo*) methylene hydrogens of the 3-membered ring is also large compared to that of the structurally related 3,4-methano-2-pyrrolidine ($\Delta\delta_H$ 0.41).[16] B3LYP/6-311+G(d,p) calculations[11] on model structure **7C** (without $Fe(CO)_4$) revealed two minima with the *i*Pr group in either the equatorial (**I**) or axial (**II**) position ($\Delta E_{ax\text{-}eq}$ = 2.0 kcal/mol) with calculated ^1H NMR chemical shifts that are similar to those observed (see Figure 3). Given the bulkiness of the $Fe(CO)_4$ group it is difficult to judge whether the equitorial or axial form of **7c** is preferred.

Attempts to synthesize 2-aza-1-phosphabicyclo[2.1.0]pentane **7d** by intramolecular phosphinidene addition to the allylic group of **6d** failed. This bicyclic structure, containing a 4- and a 3-membered ring is apparently too strained to compete against the self condensation, as reaction of **6d** with Collman's reagent resulted only in a mixture of products that we assume to consist of Fe,P-clusters as indicated by the ^{31}P NMR resonances (δ +167, -147 (J(P,P) = 275 Hz); δ+145, -137 (J(P,P) 179 Hz)). Evidence for the intermediacy of a phosphinidene iron complex was obtained by executing the reaction in the presence of 1 equivalent of phenylacetylene as trapping reagent. As expected, cycloadduct phosphirene **8d** was obtained in 56% isolated yield.





I	*endo*	*exo*	**II**	*endo*	*exo*
Calc.	1.18	-0.24	Calc.	0.97	0.04
Exp.	1.15	0.18	Exp.	1.15	0.18

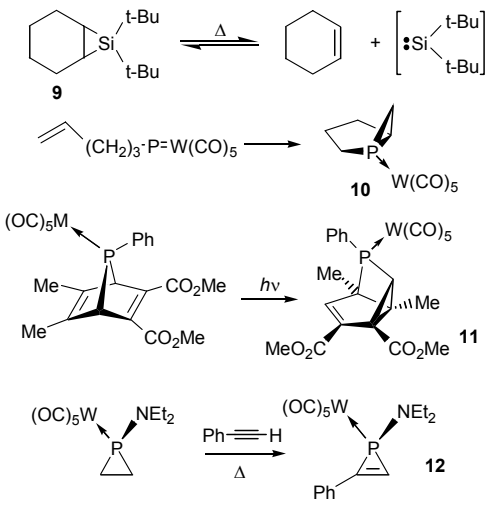
Figure 3 - B3LYP/6-311+G(d,p) conformers of **7C** with calculated and observed ^1H NMR chemical shifts for the *endo* and *exo* phosphirane protons.

If bicyclic **7d** cannot be isolated, while the transient phosphinidene complex is trappable, and as the larger structure **7a** is of limited stability, due to retroaddition and self condensation to give Fe,P-clusters, the question arises whether the remarkably stable bicyclic products **7b** and **7c** are also amenable to retroaddition. The fact that both these products undergo slow decomposition in solution would suggest such behavior. To make this more tractable we used phenylacetylene both as solvent and as trapping reagent for the retroadduct, i.e., the phosphinidene iron complex. Indeed, **7b** and **7c**

are both converted at room temperature in high (isolated) yield to the corresponding phosphirenes **8b** (57%) and **8c** (76%). As determined by ^{31}P NMR, the reaction of **7b** with a k_{obs} of 3.10^{-4} s^{-1} is about 30 times faster than that of **7c**. This observation suggests that 2-aza-1-phosphabicyclo-[3.1.0]hexane **7c** is the most stable bicyclic compound of the series.

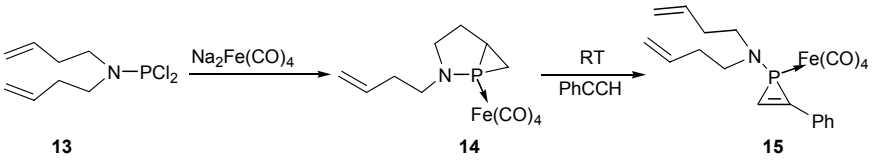
4.2.2 Dynamic behavior

In solution the bicyclic compounds undergo apparently rapid addition ↔ retroaddition of [R*i*PrNPFe(CO)$_4$] to and from the double bond, a phenomenon so far only found for the reversible extrusion (>50°C) of free silylenes from bicyclic silacyclopropanes **9**.[17] In contrast, W(CO)$_5$-complexed phosphorus compounds are stable like **10**, which is also formed intramolecularly,[18] and **11**, which is formed photochemically from its phosphanorbornadiene precursor.[19] Only at elevated temperatures (> 50°C) and in the presence of alkynes do the W(CO)$_5$-complexed aminosubstituted phosphiranes convert into phosphirenes (e.g., **12**), although slow isomeric scrambling was observed for separate isomers of one such complex at room-temperature.[6a]



Scheme 3

The dynamic addition ↔ retroaddition behavior of compounds **7a-c** would become even more evident if equivalent double bonds were to compete intramolecularly for the transient iron phosphinidene. To achieve this we reacted symmetrically substituted **13** with Collman's reagent to synthesize **14** (71%) as a stable yellow liquid. Not only are the ^{1}H, ^{13}C, and ^{31}P NMR characteristics for the bicyclic 2-aza-1-phosphabicyclo[3.1.0]hexane similar to those of **7c**, in phenylacetylene the –19 ppm ^{31}P NMR signal converts into one at –37 ppm, which is assigned to phosphirene **15**, thereby confirming the ability of **14** to undergo retroaddition.



Scheme 4

The dynamic behavior of **14** with the phosphinidene iron group exchanging between the double bonds can be shown spectroscopically. Of the various groups in the ^{1}H NMR spectrum (Figure 4a) the *endo* C*H*N (2.91 ppm) and the *endo* C*H*P (1.23 ppm) protons are readily identified by their NOE effect (Scheme 5, left-hand site). ^{1}H NMR NOE spectra at 74°C in C_6D_6 reveal magnetization transfer between the two methylene hydrogens of the phosphirane ring and the geminal hydrogens of the olefinic group.

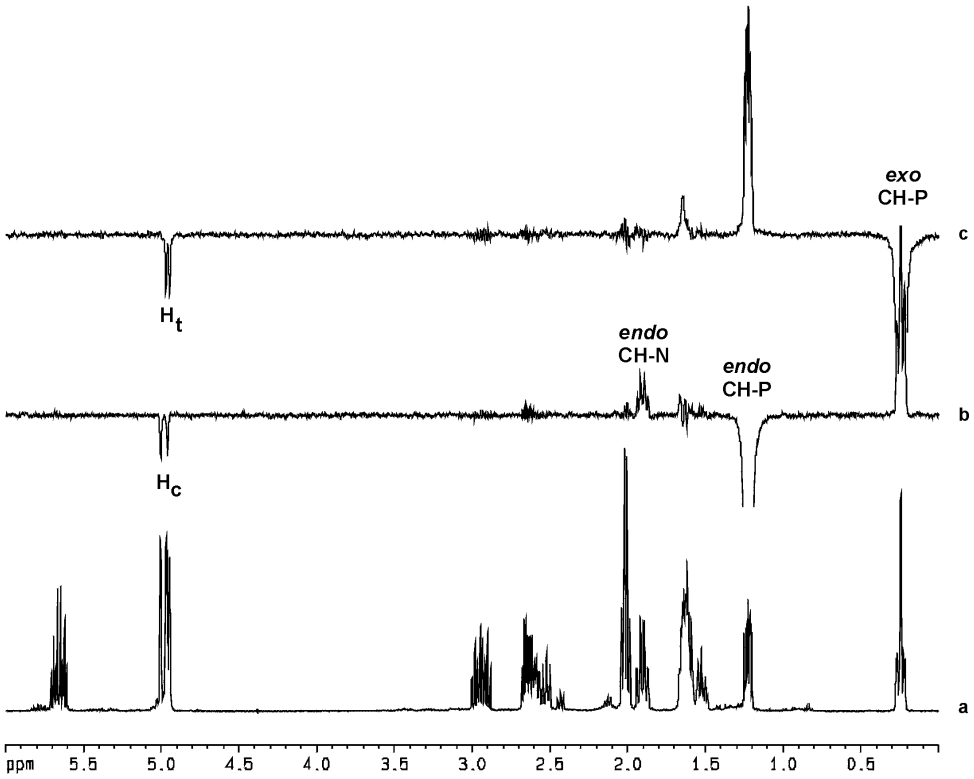
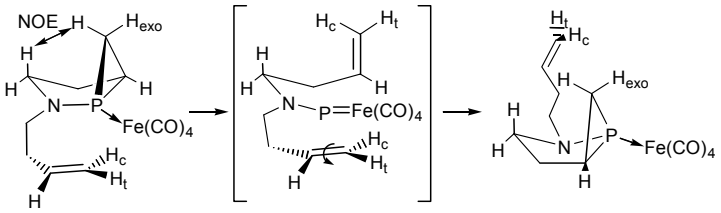


Figure 4 - Proton spectra of a solution of **14** in C_6D_6 at 74°C. a) The standard spectrum; b) and c) NOE spectra recorded after selective inversion of the signals at 1.23 ppm (b) and 0.24 ppm (c) respectively, and a mixing time of 1.5 s. Negative signals around 5 ppm are due to chemical exchange. Positive signals are due to NOE.

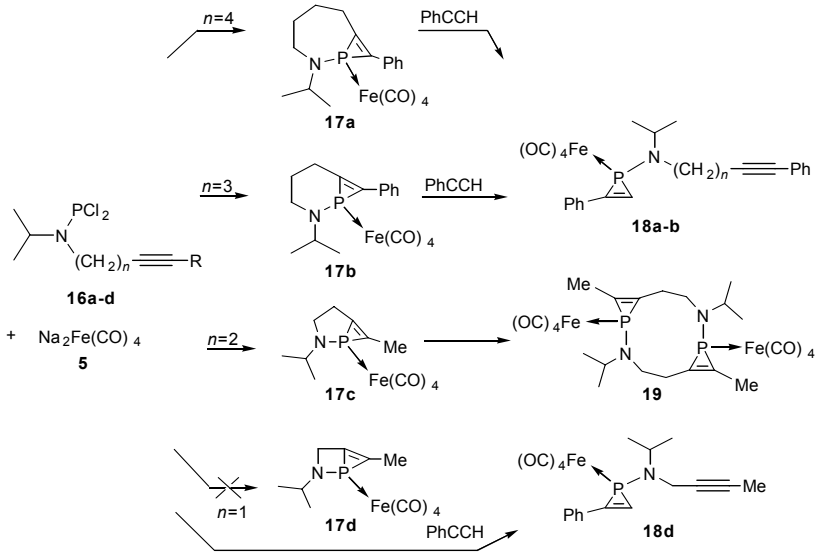
Specifically, the *endo* C*H*P hydrogen (1.23) shows magnetization transfer with the olefinic hydrogen labeled H_c (4.98) (Figure 4b) and the *exo* C*H*P hydrogen (0.24) with olefinic hydrogen H_t (4.96) (Figure 4c). These effects are best explained by shuttling of the transient phosphinidene complex between the two double bonds as illustrated in Scheme 5. Unfortunately, the rate of exchange at 74°C is too slow on the NMR time scale to acquire reliable kinetic data.



Scheme 5 - Intramolecular phosphinidene exchange in **14**.

4.2.3 Bicyclic phosphirenes

The observed behavior of bicyclic phosphiranes **7a-d** results clearly from a balance between the energy gained by phosphinidene addition offset by the accompanying increase in strain. Phosphirenes have larger strain energies than phosphiranes, but phosphinidenes have a higher affinity for a triple bond than for a double bond, as has been illustrated by their exchange. Hence, addition of $[R_2NPFe(CO)_4]$ to an internal triple bond may be expected to give similar dynamic phosphinidene behavior as discussed in the first section. Again, four cases are considered in which the alkyl chain between the nitrogen and the triple bond varies from 1 to 4 (Scheme 6).



Scheme 6 - Synthesis and reactivity of bicyclic phosphiranes **17**.

Starting with the longest chain (n = 4), reaction of **16a** with Collman's reagent gave in a remarkably good yield (60%) the first bicyclic phosphirene, 2-aza-1-phosphabicyclo-[5.1.0]oct-7-ene **17a**, as a yellow solid (m.p. 71-72°C). Its structure was confirmed with an X-ray single crystal structure determination (Figure 5).[12] The geometrical features are as expected[8b] for a phosphirene with a CPC angle of 44.39(8)°, normal P-C bonds lengths (1.7522(18), 1.7810(17) Å), and a C=C bond (1.335(2) Å) conjugated with a phenyl ring (torsion angle -0.4(3)°). Also the ^{31}P NMR chemical shift in solution at –42.3 ppm is as expected, but the slightly shielded ^{13}C NMR resonances of the phosphirene carbons (~7 ppm) suggest some increased strain as does the large ^{1}J(C,P) coupling constant for the phenyl-substituted carbon (37 Hz), being almost twice that found for other 2-phenylphosphirenes.[8b] In the crystal, the seven-membered ring adopts a twist-chair conformation[20] with the nitrogen atom deviating slightly from planarity (Σ angles 354.3°).

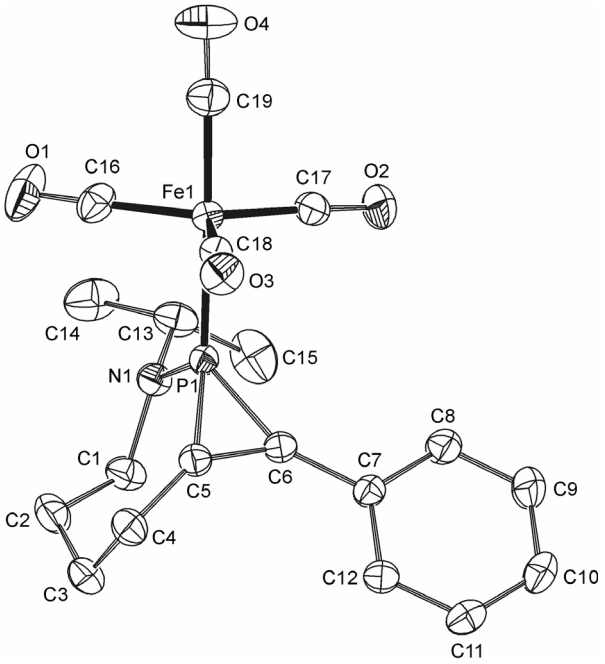


Figure 5 - Displacement ellipsoid plot (50% probability level) of **17a**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (deg) and torsion angles (deg): P1-Fe1 2.2244(5), P1-N1 1.6755(15), P1-C5 1.7522(18), P1-C6 1.7810(17), C5-C6 1.335(2), Fe1-C19 1.794(2), P1-C5-C6 68.95(11), P1-C6-C5 66.66(10), P1-Fe1-C18 90.26(6), Fe1-P1-N1 116.10(5), N1-P1-C5 107.09(8), C5-P1-C6 44.39(8), P1-C6-C7-C8 13.4(4), C5-C6-C7-C12 -0.4(3), Fe1-P1-N1-C1 -162.72(11), Fe1-P1-N1-C13 44.61(14).

The ease of formation of **17a** is quite surprising. Presuming inherent ring strain to affect the stability of the phosphirene ring, we set out to examine whether **17a** was amenable to retroaddition, a process that has been observed for other 1-aminophosphirenes only above T = 130°C,[6a] by attempting to trap the regenerated phosphinidene iron complex intermolecularly with

phenylacetylene that was also used as solvent. Gratifyingly, slow transfer was observed from **17a** (δ_P –42) to **18a** (δ_P –37) with an observed rate constant (k_{obs}) of $5 \cdot 10^{-7}$ s^{-1} at room temperature.

Next we attempted the synthesis, under dilute conditions, of the still more strained bicyclic structure 2-aza-1-phosphabicyclo[4.1.0]hept-6-ene **17b** with an alkyl chain of $n = 3$. Monitoring the reaction of Collman's reagent with **16b** by ^{31}P NMR showed its quantitative formation (δ_P –41), but isolation as a pure substance proved to be tedious (28 %, red-brown oil) due to slow decomposition and the formation of Fe,P-clusters, indicating its limited stability. All NMR data support the assignment of structure **17b**, which has characteristic resonances for the phosphirene ring, but enhanced strain as compared to **17a** may be inferred from the larger ^1J(C,P) coupling constant (45 Hz) for the phenyl substituted carbon. The much higher instability of this novel highly strained bicyclic structure is further evident from its instantaneous reaction with phenylacetylene to give 2-phenylphosphirene **18c** (δ_P –37 ppm, 12% isolated yield) besides Fe,P-clusters.

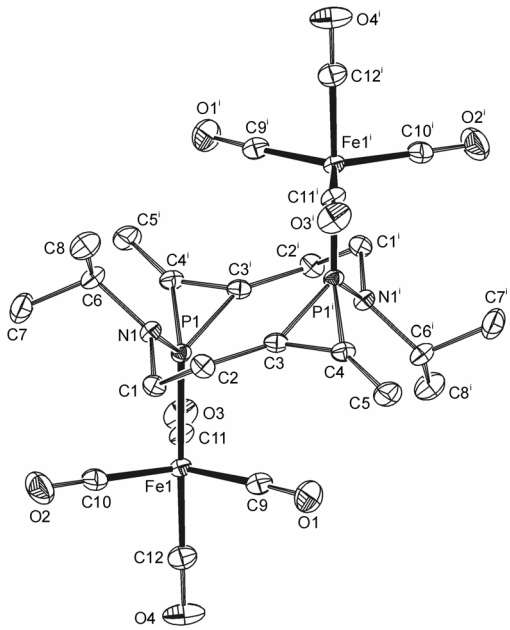


Figure 6. Displacement ellipsoid plot (50% probability level) of **19**. Hydrogen atoms are omitted for clarity. Symmetry operation i: 1-x, 1-y, 1-z. Selected bond distances (Å), angles (deg) and torsion angles (deg): P1-Fe1 2.2421(5), P1-N1 1.6841(14), P1-C3^i 1.7685(16), P1-C4^i 1.7591(16), C3-C4 1.325(2), Fe1-C12 1.7866(18), P1^i-C3-C4 67.55(10), P1^i-C4-C3 68.31(10), P1-Fe1-C11 85.98(5), Fe1-P1-N1 118.90(5), N1-P1-C3^i 114.82(7), C4^i-P1-C3^i 44.14(8), Fe1-P1-N1-C1 26.31(13), Fe1-P1-N1-C6 -124.80(10), C2-C3-C4-C5 4.8(4).

It would appear that **17b** is the most strained bicyclic phosphirene feasible. Still, we pursued the viability of the even more strained **17c** by reacting Collman's reagent with phosphine **16c**, in which a C_2H_4 unit separates the nitrogen and the methyl substituted acetylene. ^{31}P NMR showed the formation of related products (four resonances at –33 to –34.3 ppm) of which the major one (–34.3 ppm) could be isolated as a yellow solid (m.p. 124°C) albeit in low yield (8%). An X-ray crystal

structure determination[12] revealed this product (**19**) to be the unexpected dimer of bicyclic phosphirene **17c** (Figure 6). The tricyclic molecule is located on an inversion center in the crystal with a double-chair conformation for the unique 10-membered heterocyclic ring with the two *trans* $Fe(CO)_4$ groups in axial positions. In the crystal, the phosphirene rings have typical bond lengths and angles and, in solution, normal ^{13}C chemical shifts for its carbons (150, 153) and a coupling constant ($^1J(C,P) = 19.4$ Hz) for the methyl substituted one comparable to other unsymmetrical 2-substituted phosphirenes (18-22 Hz).[8b] Surprising is the triplet for the methylene carbon (C2(a)), which apparently couples with both phosphorus atoms to the same extent ($^2J(C,P) = {}^3J(C,P) = 3.7$ Hz).

The manner in which **19** is formed may be explained speculatively as follows. From **16c** an insipient phosphinidene iron complex is generated, possibly being in equilibrium with **17c** by cycloaddition, which than adds *inter*molecularly to the triple bond of another molecule of **16c**. Subsequent conversion of the PCl_2 group to a phosphinidene complex would then give **19** on ring closure. This route would also explain the likely formation of byproducts other than the P/C-clusters, such as the *cis* isomer, and higher condensation products (trimers, etc.) in more concentrated solutions.

It is then not surprising that reaction of propargylic substituted phosphine **16d** with Collman's reagent (**5**) did not result in a bicyclic product (**17d**) nor its dimer and neither in P/Fe clusters. However, because a phosphinidene iron complex is indeed generated *in situ*, as demonstrated by the formation 2-phenylphosphirene **18d** (26%) by performing the reaction in the presence of phenylacetylene, we presume that polymerization takes place in the absence of a trapping reagent.

4.3 Conclusion

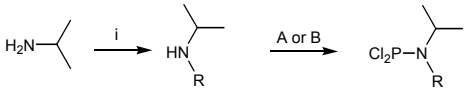
We have shown that, depending on the ring-size of the resulting bicyclic heterocycle, electrophilic phosphinidene [R*i*PrNP=$Fe(CO)_4$] can be trapped intramolecularly with double and triple bonds. The novel bicyclic 2-aza-1-phosphabicyclo[*n*.1.0]alkanes and –alkenes (*n*=3-5) show varying degrees of stability and several could be isolated in pure form. Remarkably, in all cases phosphinidene addition is reversible at room temperature; in phenylacetylene phosphinidene exchange with solvent molecules was shown to take place. Generation of a *bis*-butenyl amino phosphinidene iron complex led to an olefinic substituted phosphirane in which the phosphinidene exchange between the two double bonds was detected using dynamic NMR experiments at higher temperatures.

4.4 Experimental Part

All experiments were performed under an atmosphere of dry nitrogen. Isopropylamine and triethylamine were distilled and stored over KOH. PCl_3 was distilled prior to use. Solvents were distilled from $LiAlH_4$ (pentane, diethylether) or sodium benzophenone (THF). 1-phenyl-6-bromo-1-hexyn,[21] 1-phenyl-5-bromo-1-pentyn,[22] 5-bromo-2-pentyn[23] and isopropyl-prop-2-enylamine[24] (**20d**) were synthesized according to literature methods. The secondary amines were synthesized according to the procedure of Surzur *et al.*[24] $Na_2Fe(CO)_4.1.5$ dioxane (Collman's reagent) was purchased from Fluka or synthesized according to literature procedures.[25] All other compounds were used as purchased.

NMR spectra were recorded at 25°C (unless otherwise indicated) on Bruker AC 200 (^1H, ^{13}C), Bruker Avance 250 (^1H, ^{13}C, ^{31}P) and Bruker Avance 400 MHz (^1H, ^{13}C) spectrometers and NOE spectra (Figure 4) were recorded with a double pulsed field gradient spin echo sequence (DPFGSE).[26] NMR-chemical shifts are internally referenced to the solvent for ^1H ($CDCl_3$: 7.25 ppm, C_6D_6: 7.15 ppm) and ^{13}C ($CDCl_3$: 77.0 ppm, C_6D_6: 128 ppm) and externally for ^{31}P to 85% H_3PO_4. IR spectra

were recorded on a Mattson-6030 Galaxy FT-IR spectrophotometer and high-resolution mass spectra (HRMS) on a Finnigan MAT 900 spectrometer.



20 R: $(CH_2)_n$—CH=CH_2 **6**

21 R: $(CH_2)_n$—C≡C—R' **16**

(R' = Me, Ph)

General synthesis of the amines 20 and 21. The unsaturated group was introduced by alkylating isopropylamine (10-fold excess) with the appropriate unsaturated bromide at 50°C in the dark. After removal of isopropylamine by distillation the organic phase was treated with Et_2O and water, dried over Na_2SO_4, and concentrated. The crude product (**20**, **21**) was used without further purification or distilled, depending on the purity.

Isopropyl-hex-5-enylamine 20a. Reaction-time: 44.5h. Faint yellow liquid (91 %). b.p. 170°C/760 mm Hg; ^{13}C NMR ($CDCl_3$): δ 138.80 (s, =CH), 114.42 (s, $=CH_2$), 48.70 (s, CHN), 47.46 (s, CH_2N), 33.67 (s, =CH$\underline{C}H_2$), 29.97 (s, $\underline{C}H_2CH_2N$), 26.76 (s, $\underline{C}H_2CH_2CH_2N$), 23.03 (s, CH_3); ^{1}H NMR ($CDCl_3$,): δ 5.76 (ddt, $^3J_{HH}$(trans)=17.0 Hz, $^3J_{HH}$(cis)=10.2 Hz, $^3J_{HH}$=6.8 Hz, 1H, =CH), 4.97 (m, 2H, $=CH_2$), 2.71 (sp, $^3J_{HH}$=6.3 Hz, 1H, CHN), 2.52 (t, $^3J_{HH}$=6.8 Hz, 2H, CH_2N), 2.00 (dt, $^3J_{HH}$=6.8 Hz, $^3J_{HH}$=7.1 Hz, 2H, $C\underline{H}_2$-CH=), 1.39 (m, 4H, -$\underline{C}H_2C\underline{H}_2CH_2N$), 0.98 (d, $^3J_{HH}$=6.3 Hz, 6H, $(C\underline{H}_3)_2CH$), 0.8-0.9 (br, NH). IR (KBr): ν = 3442.6 (br), 2962.9 (m), 2928.1 (m), 1261.5 (s), 1099.5 (s), 1022.3 (s), 802.4 (s) cm^{-1}. HRMS: Calcd for $C_9H_{19}N$: 141.15175; found: 141.15283; *m/z* (%): 141 (6) [M^+], 140 (2) [M^+-H], 72 (100) [CH_2=N(H)*i*Pr$^+$].

Isopropyl-pent-4-enylamine 20b. Reaction time: 44h. Colorless liquid (96 %). b.p. 70°C/45 mm Hg. ^{13}C NMR ($CDCl_3$): δ 138.51 (s, =CH), 114.54 (s, $=CH_2$), 48.67 (s, CHN), 47.00 (s, CH_2N), 31.66 (s, $\underline{C}H_2CH$=), 29.61 (s, $\underline{C}H_2CH_2N$), 23.03 (s, $(\underline{C}H_3)_2CH$); ^{1}H NMR ($CDCl_3$): δ 5.81 (ddt, $^3J_{HH}$(trans)=17.0 Hz, $^3J_{HH}$(cis) =10.3 Hz, $^3J_{HH}$=6.6 Hz, 1H, =CH), 4.91-5.05 (m, 2H, $=CH_2$), 2.77 (sp, $^3J_{HH}$=6.2 Hz, 1H, CHN), 2.59 (t, $^3J_{HH}$=7.3 Hz, 2H, CH_2N), 2.04-2.13 (m, 2H, $C\underline{H}_2CH$=), 1.51-1.63 (m, 2H, $C\underline{H}_2CH_2N$), 1.03 (d, $^3J_{HH}$=6.2 Hz, 6H, $(C\underline{H}_3)_2CH$), 0.8-1.0 (br, NH); IR (KBr): ν = 3437.4 (w, br), 2962.9 (m), 2924.3 (m), 2852.9 (w), 1261.5 (s), 1099.5 (s), 1022.3 (s), 802.4 (s) cm^{-1}; HRMS: Calcd for $C_8H_{17}N$: 127.13610; found: 127.13616; *m/z* (%): 127 (1) [M^+], 126 (15) [M^+-H], 72 (100) [CH_2=N(H)*i*Pr$^+$].

Isopropyl-but-3-enylamine 20c. Reaction time: 90h. Colorless liquid (72 %). b.p. 131°C (35°C/42 mm Hg). ^{13}C NMR ($CDCl_3$): δ 136.59 (s, =CH), 116.26 (s, $=CH_2$), 48.55 (s, CHN), 46.44 (s, CH_2N), 34.51 (s, =CH$\underline{C}H_2$), 22.96 (s, $(\underline{C}H_3)_2CH$). ^{1}H NMR ($CDCl_3$): δ 5.77 (ddt, $^3J_{HH}$(trans)=17.2 Hz, $^3J_{HH}$(cis)=10.1 Hz, $^3J_{HH}$=6.9 Hz, 1H, =CH), 5.00-5.11 (m, 2H, $=CH_2$), 2.77 (sp, $^3J_{HH}$=6.2 Hz, 1H, NCH), 2.65 (t, $^3J_{HH}$=6.9 Hz, 2H, NCH_2), 2.23 (dt, $^3J_{HH}$=$^3J_{HH}$=6.9 Hz, 2H, $C\underline{H}_2CH$=), 1.04 (d, $^3J_{HH}$=6.2 Hz, 6H, CH_3), 0.8-1.0 (br, 1H, NH). IR (KBr): ν = 3447.0 (s, br), 2959.0 (m), 2924.3 (s), 2852.9 (m), 1261.5 (m), 1101.4 (m), 1022.3 (m), 802.4 (m) cm^{-1}. HRMS: Calcd for $C_7H_{15}N$: 113.12045; found: 113.11983; *m/z* (%): 113 (1) [M^+], 112 (7) [M^+-H], 98 (8) [M^+-CH_3], 72 (100) [CH_2=N(H)*i*Pr$^+$].

Isopropyl-(6-phenylhex-5-ynyl)amine 21a. 93 h. Colorless liquid (64%). b.p. 55-60°C/4x10^{-2} mm Hg. ^{13}C NMR ($CDCl_3$): δ 131.53 (s, *o*-ArC), 128.15 (s, *m*-ArC), 127.49 (s, *p*-ArC), 123.99 (s, *ipso*-ArC), 90.02 (s, $CH_2\underline{C}$≡), 80.80 (s, ≡$\underline{C}$Ph), 48.72 (s, CHN), 47.13 (s, CH_2N), 29.80 (s, $\underline{C}H_2CH_2N$), 26.71 (s, $\underline{C}H_2CH_2C$≡), 23.06 (s, CH_3), 19.38 (s, $\underline{C}H_2C$≡). ^{1}H NMR ($CDCl_3$): δ 7.34-7.40 (m, 2H, *o*-ArH), 7.23-7.28 (m, 3H, *m*+*p*-ArH), 2.79 (sp, $^3J_{HH}$=6.2 Hz, 1H, NCH), 2.63 (t, $^3J_{HH}$=6.2 Hz, 2H, CH_2N), 2.42 (t, $^3J_{HH}$=6.6 Hz, 2H, CH_2C≡), 1.60-1.68 (m, 4H, CH_2CH_2), 1.04 (d, $^3J_{HH}$=6.2 Hz, 6H, CH_3), 0.8-0.9 (broad, 1H, NH). IR (KBr): ν = 3441.2 (br), 2962.9 (s), 2933.9 (s), 2862.5 (m), 2231.8 (w), 1599.1 (w), 1491.1 (m), 1379.2 (m), 1331.8 (w), 1172.8 (m), 756.1 (s), 692.2 (s), 526.6 (w) cm^{-1}. HRMS: Calcd for $C_{15}H_{21}N$: 215.16739; found: 215.16883; *m/z* (%): 215 (<1) [M^+], 72 (76) [CH_2=N(H)*i*Pr$^+$], 43 (100) [$C_3H_7^+$].

Isopropyl-(5-phenylpent-4-ynyl)amine 21b. 90 h. Colorless liquid (79%). b.p. 70-80°C/1-2 mm Hg. ^{13}C NMR ($CDCl_3$): δ 131.52 (s, *o*-ArC), 128.18 (s, *m*-ArC), 127.54 (s, *p*-ArC), 123.95 (s, *ipso*-ArC), 89.72 (s, $CH_2\underline{C}$≡), 80.92 (s, ≡$\underline{C}$Ph), 48.63 (s, CHN), 46.51 (s, CH_2N), 29.32 (s, $\underline{C}H_2CH_2N$), 23.07 (s, CH_3), 17.45 (s, $\underline{C}H_2C$≡C). ^{1}H NMR ($CDCl_3$): δ 7.36-7.40 (m, 2H, *o*-ArH), 7.23-7.28 (m, 3H, *m*+*p*-ArH), 2.73-2.87 (m, 3H, $CHNCH_2$), 2.47 (t, $^3J_{HH}$=7.0 Hz, 2H,

$CH_2C\equiv$), 1.77 (quintet, $^3J_{HH}$=7.0 Hz, 2H, C$\underline{H}_2$CH$_2$N), 1.06 (d, $^3J_{HH}$=6.2 Hz, 6H, CH_3), 0.8-0.9 (broad, 1H, NH). IR (KBr): ν = 3435.4 (br), 2962.9 (m), 2361.0 (s), 2343.7 (s), 1489.1 (m), 756.1 (s), 692.5 (s) cm^{-1}. HRMS: Calcd for $C_{14}H_{19}N$: 201.15175; found: 201.15254; *m/z* (%): 201 (1) [M^+], 158 (100) [M^+- C_3H_7], 72 (76) [CH_2=N(H)*i*Pr$^+$].

Isopropyl-pent-3-ynylamine 21c. 90h. Colorless liquid (61%). b.p. 40-42°C/42 mm Hg; ^{13}C NMR ($CDCl_3$): δ 77.11 (≡$\underline{C}$CH$_2$), 76.74 (Me-$\underline{C}$≡), 48.13 (CHN), 46.10 (CH_2N), 22.97 (CH($\underline{C}H_3$)$_2$), 20.05 ($\underline{C}H_2C\equiv$), 3.48 ($\underline{C}H_3C\equiv$); ^{1}H NMR ($CDCl_3$): δ 2.81 (sp, $^3J_{HH}$=6.2 Hz, 1H, CHN), 2.70 (t, $^3J_{HH}$=6.8 Hz, 2H, CH_2N), 2.27-2.35 (m, 2H, $CH_2C\equiv$), 1.77 (t, $^5J_{HH}$=2.5 Hz, 3H, $CH_3C\equiv$), 1.05 (d, $^3J_{HH}$=6.2 Hz, 6H, (C$\underline{H}_3$)$_2$CH); IR (KBr): ν = 3427.7 (br), 2966.7 (s), 2920.4 (m), 2843.3 (w), 1176.7 (w), 1086.0 (w), 1030.1 (w), 742.6 (br), 667.4 (w) cm^{-1}; HRMS: Calcd for $C_8H_{15}N$: 125.12045; found: 125.12096; *m/z* (%): 125 (2) [M^+], 110 (96) [M^+-CH_3], 72 (100) [CH_2=N(H)*i*Pr$^+$].

Isopropyl-but-2-ynylamine 21d. A slightly different approach was used. At 0°C 1.46 g (11 mmol) 1-bromo-2-butyne was added drop-wise with stirring to 8.0 mL (110 mmol) isopropylamine. After 1 min a salt was formed. Stirring was continued for ½ hr at 0°C after which the mixture was warmed to room temperature and worked up as usual. Colorless liquid, 1.10 g (9.9 mmol, 90 %). b.p. 30-35°C/50 mm Hg; ^{13}C NMR ($CDCl_3$): δ 78.55 (s, ≡$\underline{C}$CH$_2$), 77.43 (s, Me-$\underline{C}$≡), 47.06 (s, CHN), 36.11 (s, CH_2), 22.56 (s, ($\underline{C}H_3$)$_2$CH), 3.47 ($\underline{C}H_3C\equiv$); ^{1}H NMR ($CDCl_3$): δ 3.35 (q, $^5J_{HH}$=2.4 Hz, 2H, CH_2), 2.96 (sp, $^3J_{HH}$=6.2 Hz, 1H, NCH), 1.79 (t, $^5J_{HH}$=2.4 Hz, 3H, $CH_3C\equiv$), 1.23 (broad s, 1H, NH), 1.03 (d, $^3J_{HH}$=6.2 Hz, 6H, (C$\underline{H}_3$)$_2$CH). IR (KBr): ν = 3414.2 (br), 2966.7 (m), 2924.3 (m), 2856.8 (w), 1261.5 (m), 1101.42 (m), 1028.1 (m), 802.4 (m), 669.3 (w) cm^{-1}. HRMS: Calcd for $C_7H_{13}N$: 111.10480; found: 111.10433; *m/z* (%): 111 (<1) [M^+], 110 (5) [M^+-2H], 72 (100) [CH_2=N(H)*i*Pr$^+$].

General synthesis of the dichloroaminophosphines 6, 13 and 16.

Route A: 1 Equiv. of n-BuLi (1.6 M, hexane) was added to a cold (–78°C) solution of the amine (**20**, **21**) in Et_2O (15 mL/mmol), warmed to room temperature, and then added slowly to a cold (–78°C) solution of PCl_3 (2 equiv.) in Et_2O (15 mL/mmol). Warming of the reaction mixture to room temperature, filtration, solvent evaporation, and distillation gave the desired product (**6**, **16**) as an air and light sensitive liquid.

Route B: 1 Equiv. Et_3N was added to a cold (–78°C) solution of 1.3 equiv. of PCl_3 in Et_2O (5 mL/mmol) after which the secondary amine was added dropwise, resulting in the immediate formation of a white precipitate. The reaction mixture was stirred for an additional 30 min at –78°C and for 3 hrs at room temperature and worked up to give the product (**6**, **13**, **16**) as air- and light-sensitive liquids.

Dichloro [isopropyl-(hex-5-enyl)amino]phosphine 6a. Route B, 64%. b.p. 55-60°C/1-2 mm Hg. ^{31}P NMR (C_6D_6): δ 166.96. ^{13}C NMR (C_6D_6): δ 138.44 (s, =CH), 114.97 (s, CH_2=), 51.54 (d, $^2J_{CP}$=22.9 Hz, CHN), 45.36 (d, $^2J_{CP}$=14.2 Hz, CH_2N), 33.52 (s, $\underline{C}H_2CH$=), 30.62 (d, $^3J_{CP}$=5.6 Hz, $\underline{C}H_2CH_2$N), 26.42 (s, $\underline{C}H_2CH_2C$=), 22.32 (d, $^3J_{CP}$=8.8 Hz, CH_3). ^{1}H NMR (C_6D_6): δ 5.67 (ddt, $^3J_{HH}$(trans)=16.9 Hz, $^3J_{HH}$(cis)=10.3 Hz, $^3J_{HH}$=6.6 Hz, 1H, CH=), 4.93-5.01 (m, 2H, CH_2=), 3.49-3.57 (m, 1H, NCH), 2.82-2.93 (m, 2H, CH_2N), 1.81-1.89 (2H, C$\underline{H}_2$CH=), 1.30-1.40 (m, 2H, C$\underline{H}_2$CH$_2$N), 1.06-1.18 (m, 2H, C$\underline{H}_2$CH$_2$CH=), 0.88 (d, $^3J_{HH}$=6.8 Hz, 6H, CH_3). HRMS: Calcd for $C_9H_{18}NPCl_2$: 241.05539; found: 241.05435; *m/z* (%): 241 (1) [M^+], 226 (12) [M^+-CH_3], 206 (26) [M^+-Cl], 172 (52) [H_2C=N(*i*Pr)$NPCl_2^+$].

Dichloro [isopropyl-(pent-4-enyl)amino]phosphine 6b. Route A, 85%. b.p. 54°C/1 mm Hg. ^{31}P NMR (C_6D_6): δ 167.05. ^{13}C NMR (C_6D_6): δ 137.85 (s, =CH), 115.56 (s, CH_2=), 51.79 (d, $^2J_{CP}$=23.1 Hz, NCH), 44.99 (d, $^2J_{CP}$=14.3 Hz, CH_2N), 31.30 (s, CH_2CH=), 30.34 (d, $^3J_{CP}$=5.6 Hz, $\underline{C}H_2CH_2$N), 22.24 (d, $^3J_{CP}$=8.7 Hz, ($\underline{C}H_3$)$_2$CH). ^{1}H NMR (C_6D_6): δ 5.61 (ddt, $^3J_{HH}$(trans)=16.9 Hz, $^3J_{HH}$(cis)=10.4 Hz, $^3J_{HH}$=6.6 Hz, 1H, =CH), 4.91-4.99 (m, 2H, CH_2=), 3.52 (dsp, $^3J_{HP}$=6.7 Hz, $^3J_{HH}$=6.8 Hz, 1H, NCH), 2.84-2.95 (m, 2H, CH_2N), 1.74-1.83 (m, 2H, C$\underline{H}_2$CH=), 1.38-1.51 (m, 2H, C$\underline{H}_2$CH$_2$N), 0.86 (d, $^3J_{HH}$=6.8 Hz, 6H, (C$\underline{H}_3$)$_2$CH). HRMS: Calcd for $C_8H_{16}NPCl_2$: 227.03973; found: 227.04086; *m/z* (%): 228 (3) [M^++H], 212 (12) [M^+-CH_3], 192 (100) [M^+-Cl], 172 (28) [H_2C=N(*i*Pr)$NPCl_2^+$].

Dichloro [isopropyl-(but-3-enyl)amino]phosphine 6c. Route A, 87%. b.p. 50°C/1 mm Hg. ^{31}P- NMR (C_6D_6): δ 166.70. ^{13}C- NMR (C_6D_6): δ 134.99 (s, =CH), 117.17 (s, CH_2=), 51.65 (d, $^2J_{CP}$=22.2 Hz, NCH), 44.90 (d, $^2J_{CP}$=13.9 Hz, CH_2N), 35.69 (d, $^3J_{CP}$=5.4 Hz, $\underline{C}H_2CH_2$N), 22.21 (d, $^3J_{CP}$=8.6 Hz, CH_3). ^{1}H- NMR (C_6D_6): δ 5.66 (ddt, $^3J_{HH}$(trans)=17.1 Hz, $^3J_{HH}$(cis)=10.3 Hz, $^3J_{HH}$=6.7 Hz, 1H, =CH), 4.89-4.97 (m, 2H, CH_2=), 3.45-3.61 (m, 1H, NCH), 2.90-3.01 (m, 2H, CH_2N), 2.05-2.14 (m, 2H, C$\underline{H}_2$CH$_2$N), 0.86 (d, $^3J_{HH}$=6.8 Hz, 6H, CH_3). HRMS: Calcd for $C_7H_{14}NPCl_2$: 213.02408; found: 213.02487; *m/z* (%): 213 (2) [M^+], 178 (17) [M^+-Cl], 172 (100) [H_2C=N(*i*Pr)PCl_2^+].

Dichloro [isopropyl-(prop-2-enyl)amino]phosphine 6d. Route B, 56%. b.p. 30ºC/1 mm Hg. ^{31}P NMR (C_6D_6): δ 167.29. ^{13}C NMR (C_6D_6): δ 136.30 (d, $^3J_{CP}$ =3.7 Hz, CH=), 117.22 (s, =CH_2), 51.88 (d, $^2J_{CP}$=25.5 Hz, CHN), 47.92 (d, $^2J_{CP}$=11.5 Hz, CH_2N), 22.25 (d, $^3J_{CP}$=9.6 Hz, CH_3). ^{1}H NMR (C_6D_6): δ 5.61 (ddt, $^3J_{HH}$(trans)=17.0 Hz, $^3J_{HH}$(cis)=10.2 Hz, $^3J_{HH}$=5.9 Hz, 1H, CH=), 4.87-4.97 (m, 2H, =CH_2), 3.46-3.58 (m, 3H, C<u>H</u>$_2$NC<u>H</u>), 0.89 (d, $^3J_{HH}$=6.8 Hz, 6H, CH_3). HRMS: Calcd for $C_6H_{12}NPCl_2$: 199.00845; found: 199.00513; *m/z* (%): 199 (4) [M^+], 184 (100) [M^+-CH_3], 108 (92) [$C_3H_6PCl^+$].

Dichloro[*bis*-(but-3-enyl)amino]phosphine 13: ***a) But-3-enylamine*:** 8.00 g (60 mmol) $AlCl_3$ was added to a cooled (0º) suspension of 2.28 g (60 mmol) $LiAlH_4$ in 100 mL Et_2O and stirred at 0ºC for 10 min after which a solution of 4.8 ml (58 mmol) allylcyanide in 60 mL Et_2O was added dropwise, followed by 1.5 hrs of stirring at 0ºC. The faint green mixture was made basic with 10% NaOH-solution followed by continuous extraction for four days of the water layer. Drying and solvent evaporation gave a colorless liquid, 2.65 g (37.4 mmol, 64%). ^{1}H NMR ($CDCl_3$): δ 5.76 (ddt, $^3J_{HH}$(trans)=17.1 Hz, $^3J_{HH}$(cis)=10.2 Hz, $^3J_{HH}$=6.9 Hz, 1H, CH=), 5.02-5.11 (m, 2H, CH_2=), 2.74 (t, $^3J_{HH}$=6.6 Hz, 2H, CH_2N), 2.18 (m, 2H, =CHC<u>H</u>$_2$), 1.1-1.2 (broad, 2H, NH_2). ***b) Bis-(but-3-enyl)amine:*** 2.28 g (32 mmol) but-3-enylamine, 1.12 mL (8 mmol) triethylamine and 0.80 mL (8 mmol) 4-bromo-1-butene were dissolved in 6.5 mL Et_2O and refluxed for 3 hrs. At room temperature 15 mL 4N HCl was added and the water layer was extracted with diethylether (3x10 mL), neutralized, extracted again with diethylether, made basic (pH>9) and once again extracted. The combined organic fractions were dried and evaporated. The crude product contained the desired product and some triethylamine. Since Et_3N was utilized as base in the subsequent reaction no further purification was attempted. Colorless liquid: 0.87 g (7.0 mmol, 88%). ^{13}C NMR ($CDCl_3$): δ 136.51 (s, CH=), 116.24 (s, CH_2=), 48.77 (s, CH_2N), 34.33 (s, <u>C</u>H$_2$CH=). ^{1}H NMR ($CDCl_3$):[27] δ 5.75 (ddt, $^3J_{HH}$(trans)=17.1 Hz, $^3J_{HH}$(cis)=10.2 Hz, $^3J_{HH}$=6.8 Hz, 2H, CH=), 4.96-5.11 (m, 4H, CH_2=), 2.67 (t, $^3J_{HH}$=6.9 Hz, 4H, CH_2N), 2.18-2.28 (m, 4H, =CHC<u>H</u>$_2$), 0.8-1.1 (broad, 1H, NH). ***c) Dichloro[(bis-but-3-enyl)amino]phosphine* 13:** Route B, 67%. b.p. 34-35ºC, 1-2 mm Hg. ^{31}P NMR (C_6D_6): δ 163.31. ^{13}C NMR (C_6D_6): δ 134.75 (s, CH=), 117.33 (s, CH_2=), 47.17 (d, $^2J_{CP}$=20.9 Hz, CH_2N), 32.71 (d, $^3J_{CP}$=4.0 Hz, <u>C</u>H$_2$CH$_2$N). ^{1}H NMR (C_6D_6): δ 5.47 (ddt, $^3J_{HH}$=17.0 Hz, $^3J_{HH}$=10.3 Hz, $^3J_{HH}$=6.8 Hz, 2H, CH=), 4.85-4.95 (m, 4H, CH_2=), 2.94 (dt, $^3J_{HP}$=13.0 Hz, $^3J_{HH}$=7.2 Hz, 4H, CH_2N), 1.90-1.98 (m, 4H, C<u>H</u>$_2$CH$_2$N). HRMS: Calcd $C_8H_{14}NPCl_2$: 225.0241; found: 225.0237; *m/z* (%): 225 (5) [M^+], 172 (100) [H_2C=N(*i*Pr)PCl_2^+], 130 (40) [$CH_2NPCl_2^+$].

Dichloro [isopropyl-(6-phenylhex-5-ynyl)amino]phosphine 16a. Route B, 87%. b.p. 97-105ºC/5x10^{-3} mm Hg. ^{31}P NMR (C_6D_6): δ 167.13 (d, $^3J_{PH}$=10.1 Hz). ^{13}C NMR (C_6D_6): δ 131.83 (s, *o*-ArC), 128.55 (s, *m*-ArC), 127.84 (s, *p*-ArC), 124.58 (s, *ipso*-ArC), 89.84 (s, CH_2<u>C</u>≡), 81.84 (s, ≡<u>C</u>Ph), 51.62 (d, $^2J_{CP}$=23.6 Hz, CHN), 45.02 (d, $^2J_{CP}$=13.5 Hz, CH_2N), 30.24 (d, $^3J_{CP}$=5.4 Hz, <u>C</u>H$_2$CH$_2$N), 26.22 (s, <u>C</u>H$_2$CH$_2$C≡), 22.27 (d, $^3J_{CP}$=9.0 Hz, CH_3), 19.24 (s, <u>C</u>H$_2$C≡). ^{1}H NMR (C_6D_6): δ 7.45 (m, 2H, *o*-ArH), 6.99-7.04 (m, 3H, *m*+*p*-ArH), 3.52 (dsp, $^3J_{HH}$=$^3J_{HP}$=6.8 Hz, 1H, NCH), 2.89 (dt, $^3J_{HP}$=11.3 Hz, $^3J_{HH}$=7.6 Hz, 2H, NCH_2), 2.13 (t, $^3J_{HH}$=6.9 Hz, 2H, CH_2C≡), 1.46-1.58 (m, 2H, -C<u>H</u>$_2$CH$_2$N), 1.20-1.33 (m, 2H, C<u>H</u>$_2$CH$_2$C≡), 0.88 (d, $^3J_{HH}$=6.8 Hz, 6H, CH_3). HRMS: Calcd for $C_{15}H_{20}NPCl_2$: 315.07104; found: 315.07000; *m/z* (%): 315 (6) [M^+], 280 (28) [M^+-Cl], 214 (32, [M^+-PCl_2], 198 (78) [$PhC_4H_4^+$], 156 (100) [M^+-*i*PrN(H)PCl_2].

Dichloro [isopropyl-(5-phenylpent-4-ynyl)amino]phosphine 16b. Route B, 79%. b.p. 72-75ºC/ 10^{-2} mm Hg. ^{31}P NMR ($CDCl_3$,): δ 167.52 (d, $^3J_{PH}$=10.1 Hz). ^{13}C NMR ($CDCl_3$,): δ 131.43 (s, *o*-ArC), 128.17 (s, *m*-ArC), 127.65 (s, *p*-ArC), 123.59 (s, *ipso*-ArC), 88.57 (s, CH_2<u>C</u>≡), 81.52 (s, ≡<u>C</u>Ph), 51.77 (d, $^2J_{CP}$=24.9 Hz, CHN), 44.32 (d, $^2J_{CP}$=13.1 Hz, CH_2N), 29.81 (d, $^3J_{CP}$=5.3 Hz, <u>C</u>H$_2$CH$_2$N), 22.45 (d, $^3J_{CP}$=8.8 Hz, CH_3), 17.01 (s, <u>C</u>H$_2$C≡). ^{1}H NMR (C_6D_6): δ 7.46 (d, $^3J_{HH}$=7.2 Hz, 2H, *o*-ArH), 6.94-7.04 (m, 3H, *m*+*p*-ArH), 3.43-3.59 (m, 1H, CHN), 3.06 (dt, $^3J_{HP}$=11.1 Hz, $^3J_{HH}$=7.8 Hz, 2H, NCH_2), 2.08 (t, $^3J_{HH}$=6.9 Hz, 2H, CH_2C≡), 1.53-1.65 (m, 2H, C<u>H</u>$_2$CH$_2$N), 0.86 (d, $^3J_{HH}$=6.7 Hz, 6H, CH_3). HRMS: Calcd for $C_{14}H_{18}NPCl_2$: 301.05539. Found: 301.05652. M/*z* (%): 301 (<0.5, M^+), 199 (84, [M-PhCCH]$^+$), 127 (64, [M-$C_4H_{11}NPCl_2$]$^+$), 114 (100, [PhCCH]$^+$).

Dichloro [isopropyl-(pent-3-ynyl)amino]phosphine 16c. Route A, 82%. b.p. 72ºC/4 mm Hg. ^{31}P NMR (C_6D_6): δ 164.97. ^{13}C NMR (C_6D_6): δ 78.85 (d, $^4J_{CP}$=2.5 Hz, ≡<u>C</u>CH$_2$), 76.23 (s, Me<u>C</u>≡), 51.51 (d, $^2J_{CP}$=18.2 Hz, CHN), 44.83 (d, $^2J_{CP}$=17.7 Hz, CH_2N), 21.12 (d, $^3J_{CP}$=7.3 Hz, (<u>C</u>H$_3$)$_2$CH), 22.02 (d, $^3J_{CP}$=4.8 Hz, ≡C<u>C</u>H$_2$), 3.34 (s, <u>C</u>H$_3$C≡). ^{1}H- NMR (C_6D_6): δ 3.56-3.71 (m, 1H, NCH), 3.01-3.12 (m, 2H, CH_2N), 2.11-2.20 (m, 2H, ≡C<u>C</u>H$_2$), 1.55 (t, $^5J_{HH}$=2.5 Hz, 3H, ≡C<u>C</u>H$_3$), 0.83 (d, 6H, $^3J_{HH}$=6.8 Hz, CH_3). HRMS: Calcd for $C_8H_{14}NPCl_2$: 225.0241; found: 225.02371; *m/z* (%): 225 (6) [M^+], 190 (14) [M^+-Cl], 172 (100) [H_2C=N(*i*Pr)PCl_2^+].

Dichloro [isopropyl-(but-2-ynyl)-amino] phosphine 16d. Route B, 53%. b.p. 50°C/5 mm Hg. ^{31}P NMR (C_6D_6): δ 165.67. ^{13}C NMR (C_6D_6): δ 80.67 (d, $^3J_{CP}$=1.1 Hz, ≡<u>C</u>CH$_2$), 75.87 (d, $^4J_{CP}$=4.8 Hz, Me<u>C</u>≡), 52.03 (d, $^2J_{CP}$=24.6 Hz, CHN), 34.30 (d, $^2J_{CP}$=14.9 Hz, CH$_2$N), 21.92 (d, $^3J_{CP}$=9.3 Hz, (<u>C</u>H$_3$)$_2$CH), 3.19 (s, <u>C</u>H$_3$C≡). ^{1}H NMR (C_6D_6): δ 3.68-3.78 (m, 3H, C<u>H</u>$_2$NC<u>H</u>), 1.40 (t, $^5J_{HH}$=2.3 Hz, 3H, CH$_3$C≡), 0.97 (d, $^3J_{HH}$=6.7 Hz, 6H, CH(C<u>H</u>$_3$)$_2$). HRMS: Calcd for $C_7H_{12}NPCl_2$: 211.00845; found: 211.01042; *m/z* (%): 211 (6) [M^+], 196 (100) [M^+-CH$_3$], 176 (56) [M^+-Cl].

General synthesis of bicyclic phosphiranes 7a-c and 14 and phosphirene 17a. A solution of the appropriate dichloroaminophosphine (1 mmol) in Et$_2$O (5 mL) was added to a cooled (–78°C) suspension of Collman's reagent (0.35 g, 1 mmol, Na$_2$Fe(CO)$_4$.1.5 dioxane) in Et$_2$O (10 mL). The resulting mixture was warmed to –30°C at which temperature reaction occurred, as indicated by the change in color to red, and stirred overnight. After filtration and solvent evaporation to dryness the oily residue was purified as indicated.

2-Isopropyl-2-aza-1-phosphabicyclo[5.1.0]octane tetracarbonyliron(0) 7a. Purification by flash chromatography (SiO$_2$, Et$_2$O:pentane=3:100) at –15°C gave an orange oil. Yield: 53%, (95% pure). ^{31}P NMR ($CDCl_3$): at 298 K: δ –41.34; at 220 K: δ -34.5 and -47.8. ^{13}C NMR (C_6D_6): δ 214.03 (d, $^2J_{CP}$=23.9 Hz, CO), 53.42 (d, $^2J_{CP}$=3.3 Hz, <u>C</u>H(CH$_3$)$_2$), 46.91 (d, $^2J_{CP}$=3.4 Hz, CH$_2$N), 31.34 (d, $^3J_{CP}$=4.8 Hz, <u>C</u>H$_2$CH$_2$N), 28.89 (s, <u>C</u>H$_2$CH$_2$CH$_2$N), 27.06 (d, $^1J_{CP}$=8.2 Hz, PCH), 26.79 (d, $^2J_{CP}$=3.1 Hz, <u>C</u>H$_2$CHP), 25.12 (d, $^1J_{CP}$=13.4 Hz, PCH$_2$), 21.64 (d, $^3J_{CP}$=5.2 Hz, CH$_3$), 20.61 (d, $^3J_{CP}$=2.1 Hz, CH$_3$). ^{1}H NMR ($CDCl_3$): δ 3.13-3.32 (m, 1H, <u>C</u>H(CH$_3$)$_2$), 3.05-3.14 (m, 1H, HC<u>H</u>N), 2.71-2.81 (m, 1H, <u>H</u>CHN), 2.48-2.61 (m, 1H, HC<u>H</u>CH$_2$N), 2.07-2.16 (m, 1H, HC<u>H</u>-(CH$_2$)$_2$N), 1.70-1.77 (m, 2H, HC<u>H</u>CH(P) + CH(P)), 1.34-1.64 (m, 4H, <u>H</u>CH-CH$_2$N + <u>H</u>CH-(CH$_2$)$_2$N + <u>H</u>CHCH(P) + *endo*-PCH$_2$), 1.23 (d, $^3J_{HH}$=6.7 Hz, 3H, CH$_3$), 1.12 (d, $^3J_{HH}$=6.5Hz, 3H, CH$_3$), 1.19 (br, m, 1H, *exo*-PCH$_2$). IR (KBr): ν = 2048.5 (s), 1967.5 (sh), 1930.9 (s) cm^{-1} (C≡O); HRMS: Calcd for $C_{13}H_{18}FeNPO_4$: 339.03223; found: 339.02988; EI-MS *m/z* (%): 339 (8) [M^+], 227 (42) [M^+-4CO], 124 (28) [$C_8H_{12}N^+$], 70 (100) [$C_4H_8N^+$].

2-Isopropyl-2-aza-1-phosphabicyclo[4.1.0]heptane tetracarbonyliron(0) 7b. Crystallization (Et$_2$O, -80°C) gave yellow plate-like crystals. Yield: 63%. m.p. 60-62°C (decomp). ^{31}P NMR (C_6D_6): δ -45.17. ^{13}C NMR (C_6D_6): δ 213.89 (d, $^2J_{CP}$=24.3 Hz, CO), 49.69 (d, $^2J_{CP}$=8.3 Hz, CHN), 40.29 (d, $^2J_{CP}$=4.6 Hz, CH$_2$N), 24.50 (d, $^3J_{CP}$=10.0 Hz, <u>C</u>H$_2$CH$_2$N), 23.55 (d, $^2J_{CP}$=4.3 Hz, <u>C</u>H$_2$CHP), 20.48 (d, $^3J_{CP}$=7.8 Hz, CH$_3$), 19.58 (s, CH$_3$), 18.99 (d, $^1J_{CP}$=22.9 Hz, PCH$_2$), 18.67 (d, $^1J_{CP}$=1.6 Hz, PCH). ^{1}H NMR ($CDCl_3$): δ 3.63-3.78 (m, 1H, CHN), 2.68-2.83 (m, 1H, HC<u>H</u>N), 2.51-2.64 (m, 1H, <u>H</u>CHN), 2.02-2.31 (m, 2H, C<u>H</u>$_2$CHP), 1.87-1.99 (m, 1H, CHP), 1.55-1.67 (m, 1H, HC<u>H</u>-CH$_2$N), 1.43-1.52 (m, 1H, *endo*-PCH$_2$), 1.12-1.39 (m, 1H, <u>H</u>CH-CH$_2$N), 1.09 (d, $^3J_{HH}$=6.6 Hz, 6H, (C<u>H</u>$_3$)$_2$CH), 0.82-0.91 (m, 1H, *exo*-PCH$_2$). IR (KBr): ν = 2050 (m), 1969 (sh), 1937 (s) cm^{-1} (C≡O); HRMS: Calcd for $C_{12}H_{16}O_4NPFe$: 325.01657; found: 325.01796; *m/z* (%): 325 (9) [M^+], 213 (100) [M^+-4CO], 211 (20) [M^+-4CO-2H].

2-Isopropyl-2-aza-1-phosphabicyclo[3.1.0]hexane tetracarbonyliron(0) 7c. Distillation gave a yellow liquid. Yield: 64%. b.p. 33°C/5·10^{-3} mm Hg. ^{31}P- NMR (C_6D_6): δ -20.05. ^{13}C- NMR (C_6D_6): δ 213.06 (d, $^2J_{CP}$=24.4 Hz, CO), 45.34 (d, $^2J_{CP}$=6.2 Hz, CHN), 39.27 (s, CH$_2$N), 26.07 (s, <u>C</u>H$_2$CH$_2$N), 21.35 (d, $^3J_{CP}$=12.2 Hz, CH$_3$), 17.92 (s, CH$_3$), 15.85 (d, $^1J_{CP}$=8.0 Hz, PCH), 11.25 (d, $^1J_{CP}$=26.6 Hz, PCH$_2$). ^{1}H NMR (C_6D_6): δ 3.50-3.70 (m, 1H, CHN), 2.28-2.46 (m, 1H, <u>H</u>CHN), 1.71-1.83 (m, 1H, HC<u>H</u>N), 1.42-1.62 (m, 3H, C<u>H</u>$_2$C<u>H</u>P), 1.11-1.19 (m, 1H, *endo*-PCH$_2$), 0.85 (d, $^3J_{HH}$=6.7 Hz, 3H, CH$_3$), 0.77 (d, $^3J_{HH}$=6.6 Hz, 3H, CH$_3$), 0.18 (ddd, $^2J_{HH}$=$^3J_{HH}$=9.8 Hz, $^2J_{HP}$=2.7 Hz, 1H, *exo*-PCH$_2$). IR (KBr): ν = 2056 (s), 1981 (sh), 1942 (s) cm^{-1} (C≡O); HRMS: Calcd for $C_{11}H_{14}FeNO_4P$: 311.00157, Found: 311.00092; *m/z* (%): 311 (8) [M^+], 199 (100) [M^+-4CO], 157 (46) [M^+-4CO-C_3H_6], 128 (40) [M^+-4CO-C_4H_9N]; elemental analysis calcd (%) for $C_{11}H_{14}FeNO_4P$: C 42.47, H 4.54; found: C 42.50, H 4.65.

2-(But-3-enyl)-2-aza-1-phosphabicyclo[3.1.0]hexane tetracarbonyliron(0) 14. Distillation gave a yellow liquid. Yield: 71%. b.p. 30-33^{0}C/5·10^{-3} mm Hg. ^{31}P- NMR ($CDCl_3$): δ -19.18. ^{13}C NMR ($CDCl_3$): δ 212.63 (d, $^2J_{CP}$=23.9 Hz, CO), 135.40 (s, CH=), 116.74 (s, CH$_2$=), 47.38 (s, CH$_2$N(ring)), 46.37 (d, $^2J_{CP}$=5.2 Hz, CH$_2$N), 32.87 (d, $^3J_{CP}$=7.6 Hz, <u>C</u>H$_2$C=) 26.76 (d, $^2J_{CP}$=3.0 Hz, <u>C</u>H$_2$CH$_2$N(ring)), 17.10 (d, $^1J_{CP}$=6.9 Hz, PCH), 11.47 (d, $^1J_{CP}$=26.0 Hz, PCH$_2$). ^{1}H NMR ($CDCl_3$): δ 5.79 (ddt, $^3J_{HH}$(trans)=17.1 Hz, $^3J_{HH}$(cis)=10.2 Hz, $^3J_{HH}$=6.9 Hz, CH=), 5.09 (dd, $^2J_{HH}$=1.4 Hz, $^3J_{HH}$=17.1 Hz, =CH$_{trans}$), 5.04 (m, =CH$_{cis}$), 3.06-3.22 (m, 2H, C<u>H</u>NC<u>H</u>), 2.81-2.89 (m, 1H, -C<u>H</u>N), 2.50-2.57 (m, 1H, ring-C<u>H</u>N-*endo*), 2.81-2.43 (m, 4H, C<u>H</u>$_2$CH$_2$NCH$_2$C<u>H</u>$_2$), 2.11 (m, 1H, CHP), 1.75 (m, 1H, PCH$_2$-*endo*), 0.61 (ddd, $^3J_{HH}$=9.8 Hz, $^2J_{HP}$=9.8 Hz, $^2J_{HH}$=2.7

Hz, PCH_2-*exo*). IR (KBr): ν = 2056.25 (s), 1952.08 (s) cm^{-1} (C≡O); HRMS: Calcd $C_{11}H_{14}FeNO_3P$: 295.0061; found: 295.0071 [M^+–CO]. *m/z* (%): 295 (19) [M^+-CO], 211 (100) [M^+-4CO].

8-Phenyl-2-isopropyl-2-aza-1-phosphabicyclo[5.1.0]oct-7-ene tetracarbonyliron(0) 17a. Purification by flash column chromatography at –15°C (SiO_2, 6.7% Et_2O in pentane, R_f=0.46). Yield: yellow oil (60%). Crystallization (Et_2O, -80°C): bright yellow plate-like crystals. m.p. 70-71°C (decomp). ^{31}P NMR (C_6D_6): δ -42.56. ^{13}C NMR (C_6D_6): δ 214.27 (d, $^2J_{CP}$=24.6 Hz, CO), 147.84 (d, $^1J_{CP}$=37.0 Hz, =CPh), 143.32 (d, $^1J_{CP}$=5.5 Hz, CH_2C=), 130.19 (s, *p*-ArC), 129.85 (d, $^2J_{CP}$=2.4 Hz, *ipso*-ArC), 129.51 (d, $^3J_{CP}$=3.9 Hz, *o*-ArC), 129.37 (s, *m*-ArC), 47.13 (d, $^2J_{CP}$=10.2 Hz, CHN), 43.54 (d, $^2J_{CP}$=5.1 Hz, CH_2N), 31.87 (CH_2CH_2N), 27.46 (d, $^2J_{CP}$=2.6 Hz, CH_2C=), 26.57 (s, CH_2CH_2C=), 21.02 (d, $^3J_{CP}$=9.9 Hz, CH_3), 20.48 (s, CH_3). ^1H NMR (C_6D_6): δ 7.48 (d, $^3J_{HH}$=7.1 Hz, 2H, *o*-ArH), 7.09 (m, 2H, *m*-ArH), 7.01 (m, 1H, *p*-ArH), 4.14-4.24 (m, 1H, NCH), 2.90 (dddd, $^3J_{HP}$=29.1 Hz, $^2J_{HH}$=13.0 Hz, $^3J_{HH}$=5.4 Hz, $^3J_{HH}$=2.0 Hz, 1H, HCC=), 2.40-2.54 (m, 2H, H(CH)N+HCC=), 1.46-1.62 (m, 3H, H(CH)N + H(CH)CH_2N + H(CH)CH_2CH_2N), 0.75-1.03 (m, 2H, H(CH)CH_2N + H(CH)CH_2CH_2N), 0.93 (d, $^3J_{HH}$=6.6 Hz, 3H, CH_3), 0.80 (d, $^3J_{HH}$=6.7 Hz, CH_3). IR (KBr): ν = 2048.5 (s), 1967.5 (sh), 1940.5 (s) cm^{-1} (C≡O); HRMS: Calcd for $C_{19}H_{20}FeNPO_4$: 413.04791; found: 413.04596; *m/z* (%): 413 (<1) [M^+], 301 (20) [M^+-4CO], 105 (65) [$C_4H_{10}NP^+$], 72 (69) [$C_4H_{10}N^+$], 55 (66) [$C_3H_5N^+$], 41 (100) [$C_3H_5^+$].

7-Phenyl-2-isopropyl-2-aza-1-phosphabicyclo[4.1.0]hept-6-ene tetracarbonyliron(0) 17b. A cooled (-10°C) solution of 0.61 g (2.0 mmol) **16b** in 65 mL Et_2O was added dropwise in 2.5 hrs to a cooled (-10°C) suspension of 0.78 g (2.3 mmol) Collman's reagent in 20 mL Et_2O. The solution was warmed up to 0°C, stirred for 45 min and concentrated, filtered and evaporated to dryness at 0°C. Purification by column chromatography at –15°C (SiO_2, 6% Et_2O in pentane, R_f=0.30). Unstable red-brown oil, 0.22 g (0.56 mmol, 28 %, 95% pure). ^{31}P NMR (C_6D_6): δ -41.15. ^{13}C NMR (C_6D_6): δ 214.13 (d, $^2J_{CP}$=24.5 Hz, CO), 154.64 (d, $^1J_{CP}$=48.6 Hz, =CPh), 146.62 (d, $^1J_{CP}$=6.0 Hz, CH_2C=), 130.20 (s, *p*-ArC), 129.37 (s, *m*-ArC), 129.15 (d, $^3J_{CP}$=3.1 Hz, *o*-ArC), 46.32 (d, $^2J_{CP}$=5.5 Hz, CHN), 40.21 (d, $^2J_{CP}$=5.1 Hz, CH_2N), 31.72 (d, $^2J_{CP}$=8.6 Hz, CH_2C=), 28.00 (s, CH_2CH_2N), 20.22 (d, $^3J_{CP}$=10.3 Hz, CH_3), 20.04 (s, CH_3). ^1H NMR (C_6D_6), not all assignments could be made due to instability of the product: δ 7.47 (d, $^3J_{HH}$=7.1 Hz, 2H, *o*-ArH), 7.01-7.15 (m, 3H, *m*+*p*-ArH), 3.77-3.87 (m, 1H, CHN), 2.75-2.83 (m, 1H), 2.3-2.7 (m, 1H), 1.98-2.07 (m, 1H), 1.77-1.83 (m, 2H), 1.21-1.29 (m, 1H), 0.81 (d, $^3J_{HH}$=6.5 Hz, 3H, CH_3), 0.71 (d, $^3J_{HH}$=6.6 Hz, 3H, CH_3).

Phosphinidene exchange reactions in phenylacetylene.

1-(Isopropyl-(pent-4-enyl)amino)-2-phenylphosphirene tetracarbonyliron(0) 8b. The reaction of 0.23 g (0.70 mmol) of **8b** with 1.9 ml (17 mmol) phenylacetylene at room temperature in the dark, monitored by ^{31}P NMR, gave after 4h, after removal in vacuo of the solvent, 0.37 g of crude product. Chromatography (SiO_2, 3% Et_2O in pentane) at –15°C gave 0.17 g (0.40 mmol, 57%) of **8b** as orange oil. ^{31}P NMR (C_6D_6): δ -36.34. ^{13}C NMR (C_6D_6): δ 214.05 (d, $^2J_{CP}$=24.2 Hz, CO), 159.03 (d, $^1J_{CP}$=19.3 Hz, PhC=), 139.85 (s, CH_2=CH), 135.08 (d, $^1J_{CP}$=2.0 Hz, =C(P)H), 131.31 (s, *p*-ArC), 129.36 (s, *m*-ArC), 129.31 (d, $^3J_{CP}$=3.8 Hz, *o*-ArC), 127.92 (s, *ipso*-ArC), 115.15 (s, CH_2=), 48.20 (d, $^2J_{CP}$=10.5 Hz, CHN), 40.82 (d, $^2J_{CP}$=1.4 Hz, CH_2N), 32.30 (d, $^3J_{CP}$=1.4 Hz, CH_2CH_2N), 31.34 (s, CH_2C=), 21.67 (d, $^3J_{CP}$=6.6 Hz, CH_3), 21.28 (d, $^3J_{CP}$=3.8 Hz, CH_3). ^1H NMR (C_6D_6): δ 8.05 (d, $^2J_{HP}$=16.0 Hz, 1H, =C(P)H), 7.54-7.49 (m, 2H, *o*-ArH), 6.99-7.05 (m, 3H, *m*+*p*-ArH), 5.45-5.61 (m, 1H, CH_2=CH), 4.82-4.91 (m, 2H, CH_2=), 4.11 (dsp, $^2J_{HP}$=$^3J_{HH}$=6.7 Hz, 1H, CHN), 2.34 (m, 2H, CH_2N), 1.64-1.74 (m, 2H, CH_2CH=), 1.26-1.35 (m, CH_2CH_2N), 0.89 (d, $^3J_{HH}$=6.7 Hz, CH_3), 0.88 (d, $^3J_{HH}$=6.7 Hz, CH_3). IR (KBr): ν = 2050.5 (s), 1973.3 (sh), 1940.5 (s) cm^{-1} (C≡O); HRMS: Calcd for $C_{18}H_{22}FeNO_2P$: 371.0737; found: 371.07066 [M^+–2CO]; *m/z* (%): 371 (4) [M^+-2CO], 315 (100) [M^+-4CO], 102 (45) [$PhCCH^+$].

1-(Isopropyl-(but-3-enyl)amino)-2-phenylphosphirene tetracarbonyliron(0) 8c. A similar procedure was followed as described for **8b**. The reaction was completed after 6 days to give 76% of **8c** as an orange oil. ^{31}P NMR (C_6D_6): δ -36.51. ^{13}C NMR ($CDCl_3$): δ 213.51 (d, $^2J_{CP}$=24.2 Hz, CO), 159.00 (d, $^1J_{CP}$=20.7 Hz, PhC=), 135.01 (s, CH_2=CH), 134.31 (s, =C(P)H), 131.29 (s, *p*-ArC), 129.24 (d, $^3J_{CP}$=4.3 Hz, *o*-ArC), 129.23 (s, *m*-ArC), 127.66 (s, *ipso*-ArC), 116.59 (s, CH_2=), 47.98 (d, $^2J_{CP}$=10.5 Hz, CHN), 40.65 (s, CH_2N), 37.39 (s, =CCH_2), 21.82 (d, $^3J_{CP}$=6.7 Hz, CH_3), 21.38 (d, $^3J_{CP}$=3.1 Hz, CH_3). ^1H NMR (C_6D_6): δ 8.04 (d, $^2J_{HP}$=16.1 Hz, 1H, =C(P)H), 7.44-7.49 (m, 2H, *o*-ArH), 6.99-7.08 (m, 3H, *m*+*p*-ArH), 5.47 (ddt, $^3J_{HH}$(trans)=17.0 Hz, $^3J_{HH}$(cis)=10.3 Hz, $^3J_{HH}$=6.8 Hz, 1H, CH_2=CH), 4.80-4.91 (m, 2H, CH_2=), 4.05-4.15 (m, 1H, CHN), 2.34-2.47 (m, 2H, CH_2N), 1.89-1.98 (m, 2H, CH_2CH=), 0.87 (d, $^3J_{HH}$=6.7 Hz, 3H, CH_3), 0.86 (d, $^3J_{HH}$=6.7 Hz, 3H, CH_3). IR (KBr): ν = 2052.4 (s), 2015.7 (sh), 1965.6 (sh), 1944.4 (s) cm^{-1} (C≡O); HRMS: Calcd for

$C_{18}H_{20}FeNO_3P$: 385.0530; found: 385.05109 [M^+–CO]; m/z (%): 385 (5) [M^+-CO], 301 (64) [M^+-4CO], 199 (100) [M^+-4CO-PhCCH], 102 (73) [PhCCH$^+$].

1-(Isopropyl-(prop-2-enyl)amino)-2-phenylphosphirene tetracarbonyliron(0) 8d. A solution of dichloroaminophosphine **6d** (1 mmol) and phenylacetylene (0.95 mmol) in Et_2O (2.5 mL) was added to a cooled (–78°C) suspension of Collman's reagent (0.33 g, 0.95 mmol) in Et_2O (20 mL). The resulting mixture was warmed to –30°C at which temperature reaction occurred, as indicated by the color change to red. Filtration at 0°C, concentration to 1 mL, and flash chromatography over silica (3% Et_2O in pentane) at –5°C gave 213 mg (0.53 mmol, 56%) of **8d** as a red oil. ^{31}P NMR ($CDCl_3$): δ -34.74. ^{13}C NMR ($CDCl_3$): δ 213.44 (d, $^2J_{CP}$=24.2 Hz, CO), 158.68 (d, $^1J_{CP}$=19.7 Hz, Ph<u>C</u>=), 137.87 (s, CH_2=<u>C</u>H), 134.91 (s, PhC=<u>C</u>H), 131.21 (s, *p*-ArC), 129.24 (d, $^3J_{CP}$=4.6 Hz, *o*-ArC), 129.18 (s, *m*-ArC), 127.87 (s, *ipso*-ArC), 115.57 (s, CH_2=), 48.10 (d, $^2J_{CP}$=10.4 Hz, CHN), 43.37 (s, CH_2N), 21.65 (d, $^3J_{CP}$=6.7 Hz, CH_3), 21.30 (d, $^3J_{CP}$=2.7 Hz, CH_3). ^{1}H NMR ($CDCl_3$): δ 8.66 (d, $^2J_{HP}$=15.5 Hz, 1H, =C(P)H), 7.47-7.65 (m, 5H, ArH), 5.59-5.74 (m, 1H, CH_2=C<u>H</u>), 5.03-5.17 (m, 2H, CH_2=), 4.09-4.26 (m, 1H, CHN), 3.18-3.43 (m, 2H, CH_2N), 1.10 (d, $^3J_{HH}$=6.0 Hz, 6H, CH_3). IR (KBr): ν = 2050.5 (s), 1971.4 (sh), 1942.4 (s) cm^{-1} (C≡O); HRMS: Calcd for $C_{17}H_{18}FeNO_3P$: 371.0374; found: 371.03446 [M^+–CO]; m/z (%): 371 (15) [M^+-CO], 287 (70) [M^+-4CO], 183 (100) [M^+-4CO-C_8H_8], 102 (50) [PhCCH$^+$].

1-(Isopropyl-(5'-phenylpent-4'-ynyl)amino)-2-phenylphosphirene tetracarbonyliron (0) 18b. A cooled (-10°C) solution of 0.30 g (1.0 mmol) **16b** in 35 mL Et_2O was added dropwise in 2.5 hrs to a cooled (-10°C) suspension of 0.31 g (1.0 mmol) Collman's reagent in 35 mL Et_2O. The solution was warmed up to 0°C, stirred for 45 min and concentrated, filtered and evaporated to a minimal volume at 0°C. Phenylacetylene (4 mL) was added and after 10 min stirring at room-temperature removed under high vacuum at 35°C. Purification by flash column chromatography (SiO_2, 5% Et_2O in pentane). Red-brown oil: 53 mg (0.11 mmol, 12 %). ^{31}P NMR ($CDCl_3$): δ -36.28. ^{13}C NMR ($CDCl_3$): δ 213.44 (d, $^2J_{CP}$=24.1 Hz, CO), 159.08 (d, $^1J_{CP}$=23.2 Hz, =<u>C</u>-Ph), 133.82 (s, HC=), 131.44 (s, *o*-Ar-C≡), 131.22 (s, *p*-Ar-C=), 129.19 (d, $^3J_{CP}$=4.6 Hz, *o*-Ar-C=), 129.16 (s, *m*-Ar-C=), 128.23 (s, *m*-Ar-C≡), 127.68 (s, *p*-Ar-C≡), 127.60 (d, $^2J_{CP}$=2.9 Hz, *ipso*-Ar-C=), 123.65 (s, *ipso*-Ar-C≡), 89.02 (s, CH_2<u>C</u>≡), 81.29 (s, ≡<u>C</u>Ph), 47.94 (d, $^2J_{CP}$=10.7 Hz, CHN), 40.09 (s, CH_2N), 31.54 (s, <u>C</u>H_2CH_2N), 21.83 (d, $^3J_{CP}$=7.7 Hz, CH_3), 21.17 (d, $^3J_{CP}$=2.6 Hz, CH_3), 16.76 (s, <u>C</u>H_2C≡). ^{1}H NMR ($CDCl_3$): δ 8.78 (d, $^2J_{HP}$=16.3 Hz, 1H, =C(P)H), 7.61-7.65 (m, 2H, =C-(*o*-ArH)), 7.46-7.48 (m, 3H, =C-(*m*+*p*-ArH)), 7.35-7.38 (m, 2H, ≡C-(*o*-ArH)), 7.28-7.31 (m, 3H, ≡C-(*m*+*p*-ArH)), 4.15-4.26 (m, 1H, CHN), 2.73-2.86 (m, 1H, 2H, CH_2N), 2.24-2.42 (m, 2H, CH_2C≡), 1.61-1.73 (m, 2H, C<u>H</u>$_2$$CH_2$N), 1.18 (d, $^3J_{HH}$=6.8 Hz, 3H, CH_3), 1.14 (d, $^3J_{HH}$=6.9 Hz, 3H, CH_3). IR (KBr): ν = 2050.5 (s), 1973.3 (sh), 1930.9 (s) cm^{-1} (C≡O); HRMS: Calcd for $C_{23}H_{24}FeNPO$: 417.0945; found: 417.0907 [M^+–3CO]; m/z (%): 417 (12) [M^+-3CO], 387 (20) [M^+-4CO], 159 (42) [M^+-4CO-$C_{18}H_{12}$], 102 (100) [PhCCH$^+$].

1-(Isopropyl-(but-2-ynyl)amino)-2-phenylphosphirene tetracarbonyliron(0) 18d. A solution of 0.41 g (1.2 mmol) **16d** was added to a cooled (-78°C) suspension of 0.41 g (1.2 mmol) Collman's reagent and 0.13 mL (1.2 mmol) phenylacetylene in 25 mL Et_2O. The reaction mixture was warmed to –30°C and warmed up to room-temperature overnight. Filtration, solvent evaporation and flash column chromatography at 5°C (SiO_2, 5% Et_2O in pentane) yielded a red-brown oil, 110 mg, (0.27 mmol, 23%). ^{31}P NMR ($CDCl_3$): δ -34.48. ^{13}C NMR ($CDCl_3$,): δ 213.34 (d, $^2J_{CP}$=24.1 Hz, CO), 161.11 (d, $^1J_{CP}$=18.3 Hz, =<u>C</u>Ph), 134.24 (s, =CH), 131.08 (s, *p*-Ar), 129.35 (d, $^3J_{CP}$=4.8 Hz, *o*-Ar), 129.00 (s, *m*-Ar), 128.14 (s, *ipso*-Ar), 79.37 (s, ≡<u>C</u>CH_2), 78.18 (s, $^4J_{CP}$=2.3 Hz, Me<u>C</u>≡), 48.51 (d, $^2J_{CP}$=8.1 Hz, CHN), 31.53 (s, CH_2N), 21.42 (d, $^3J_{CP}$=3.5 Hz, CH_3), 21.32 (s, CH_3), 3.15 (s, <u>C</u>H_3C≡). ^{1}H NMR ($CDCl_3$): δ 8.75 (d, $^2J_{HP}$=15.7 Hz, 1H, =C(P)H), 7.48-7.72 (m, 5H, ArH), 4.02 (m, 1H, CHN), 3.52 (m, 2H, CH_2N), 1.52 (s, 3H, ≡CCH_3), 1.17 (d, $^3J_{HH}$=6.6 Hz, 3H, CH_3), 1.11 (d, $^3J_{HH}$=6.6 Hz, 3H, CH_3). IR (KBr): ν = 2052.4 (s), 1979.1 (s), 1930.9 (s) cm^{-1} (C≡O); HRMS: Calcd for $C_{18}H_{18}FeNO_3P$: 383.03737; found: 383.03945 [M^+-CO]; m/z (%): 383 (3) [M^+-CO], 299 (100) [M^+-4CO], 197 (52) [M^+-4CO-PhC=CH].

2,8-Diisopropyl-6,12-dimethyl-2,8-aza-1,7-diphosphatricyclo-[9.1.0.0^{5,7}]-dodeca-5,11-diene bis(tetracarbonyliron(0)) 19. A cooled (-30°C) solution of 0.45 g (2.0 mmol) **16c** in 50 mL Et_2O was added dropwise in 35 min to a cooled (-20°C) suspension of 0.70 g (2.0 mmol) Collman's reagent in 25 mL. Filtration, solvent evaporation and column chromatography (SiO_2, Et_2O:pentane=3:100) yielded a yellow solid (8%). Crystallization (Et_2O, -78°C) gave small, plate-like yellow crystals. m.p. 124°C (decomp.) ^{31}P NMR (C_6D_6): δ -35.30. ^{13}C NMR (C_6D_6): δ 214.09 (d, $^2J_{CP}$=24.0 Hz, CO), 153.34 (d, $^1J_{CP}$=19.4 Hz, =<u>C</u>Me), 150.44 (s, <u>C</u>=CMe), 48.95 (d, $^2J_{CP}$=9.4 Hz, CHN), 39.42 (s, CH_2N), 28.68 (t, $^2J_{CP}$=$^3J_{CP}$=3.7 Hz, <u>C</u>H_2C=), 22.28 (d, $^3J_{CP}$=9.0 Hz, <u>C</u>H_3CH), 20.28 (d, $^3J_{CP}$=1.8 Hz, <u>C</u>H_3CH), 11.39 (d, $^2J_{CP}$=2.8 Hz,

=C<u>C</u>H$_3$). ^{1}H NMR (C_6D_6): δ 3.86-4.02 (m, 2H, CHN), 2.45-2.72 (m, 4H, CH_2N), 2.23-2.41 (m, 4H, CH_2C=), 1.87 (d, $^3J_{HP}$=10.5 Hz, 6H, =CCH_3), 0.96 (d, $^3J_{HH}$=6.8 Hz, 6H, CH_3), 0.94 (d, $^3J_{HH}$=6.6 Hz, 6H, CH_3). IR (KBr): ν = 2045 (s), 1954 (s), 1929 (s) cm^{-1} (C≡O); HRMS: Calcd for $C_{22}H_{28}Fe_2N_2O_6P_2$: 590.0121; found 590.0096 [M^+-2CO]; *m/z* (%): 590 (4) [M^+-2CO], 506 (46) [M^+-5CO], 478 (10) [M^+-6CO], 422 (100) [M^+-8CO].

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3.5 Notes and References

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[12] Crystal structure determinations: X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (λ=0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å^{-1}. The structures were solved with automated Patterson methods[28] and refined with SHELXL97[29] against F^2 of all reflections. Illustrations, structure calculations and checking was performed with the PLATON package.[30]

Compound **7b**: $C_{12}H_{16}FeNO_4P$, *Fw* 325.08, yellow plate, 0.30 × 0.24 × 0.12 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 8.2860(1), b = 14.8128(2), c = 11.8843(1) Å, β = 94.1417(5)°, V = 1454.86(3) Å^3, Z = 4, D_{calc} = 1.484 g/cm^3. 23129 measured reflections of which 3326 were unique. Absorption correction based on multiple measured reflections (μ = 1.15 mm^{-1}, correction range 0.59-0.87). Non hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined freely with isotropic displacement parameters. 236 refined parameters, no restraints. *R*-indices [$I>2\sigma(I)$]: R_1 = 0.0277, wR_2 = 0.0609. *R*-indices [all refl.]: R_1 = 0.0456, wR_2 = 0.0683. S = 1.077. Residual electron density between -0.28 and 0.37 e/Å^3.

Compound **17a**: $C_{19}H_{20}FeNO_4P$, *Fw* 413.18, yellow block, 0.30 × 0.15 × 0.15 mm^3, triclinic, $P\overline{1}$ (no. 2), a = 8.6320(2), b = 10.8710(3), c = 11.4937(3) Å, α = 98.1520(14), β = 111.7000(18), γ = 91.9060(9)°, V = 987.68(5) Å^3, Z = 2, D_{calc} = 1.389 g/cm^3, μ = 0.87 mm^{-1}. 14258 measured reflections of which 4459 were unique. An absorption correction was not considered necessary. Non hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent parameter of their carrier atoms. 237 refined parameters, no restraints. *R*-indices [$I>2\sigma(I)$]: R_1 = 0.0340, wR_2 = 0.0841. *R*-indices [all refl.]: R_1 = 0.0470, wR_2 = 0.0897. S = 1.031. Residual electron density between -0.48 and 0.45 e/Å^3.

Compound **19**: $C_{24}H_{28}Fe_2N_2O_8P_2$, *Fw* 646.12, colorless plate, 0.36 × 0.27 × 0.12 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 9.6901(7), b = 15.5833(15), c = 10.2081(9) Å, β = 113.803(6)°, V = 1410.3(2) Å^3, Z = 2, D_{calc} = 1.521 g/cm^3. 15476 measured reflections of which 3229 were unique. Absorption correction based on multiple measured reflections (μ = 1.19 mm^{-1}, correction range 0.65-0.87). Non hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent parameter of their carrier atoms. 175 refined parameters, no restraints. *R*-indices [I>2σ(I)]: R_1 = 0.0267, wR_2 = 0.0618. R-indices [all refl.]: R_1 = 0.0360, wR_2 = 0.0648. S = 1.090. Residual electron density between -0.27 and 0.34 e/Å^3.

CCDC-256107 (**7b**), 256108 (**17a**) and 256109 (**19**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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Chapter 5

G3(MP2) Ring Strain in Bicyclic Phosphorus Heterocycles and Their Hydrocarbon Analogues

Mark L.G. Borst, Andreas W. Ehlers and Koop Lammertsma

J. Org. Chem. **2005**, *70*, 8110-8116

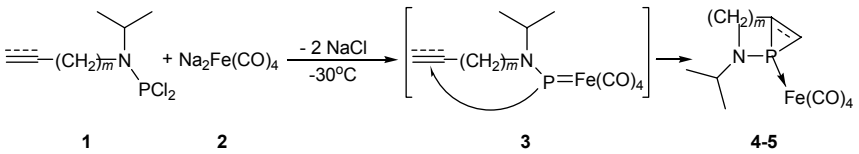
5.1 Introduction

The chemistry of phosphorus-containing rings is undergoing a rejuvenation with the recent discoveries of stable 2,4-diphosphacyclobutane-1,3-diyls,[1-2] their diboradiphospha analogues,[3] and *P*-heterocyclic carbenes.[4] Addition of electrophilic phosphinidenes to unsaturated bonds[5] is a powerful method to obtain such small rings as in 2,3-dihydrophosphasiletes,[6] phospha[3]radialanes,[7] and 7-phosphatriangulane.[8]

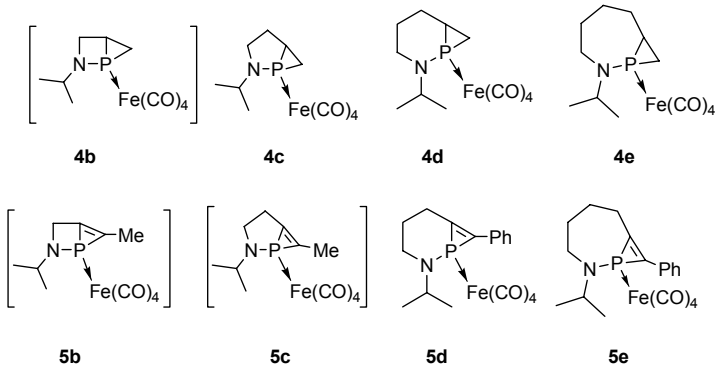
Strain is often invoked to explain the stability and/or reactivity of these ring structures. Using homodesmotic reactions[9] accurate theoretical estimates can be obtained for strain energies that compare well to experimentally determined values. Significant efforts have been devoted to obtain

strain energies for three-[10] and four-membered (un)saturated heterocyclic rings,[11-12] but relatively little is known about bicyclic structures.[13-14] In our continuing quest for novel systems we now present ring strain energies for phospha[*n*.1.0]bicycloalka(e)nes and the corresponding hydrocarbons.

Our interest in this specific bicyclic system was inspired by our recent report on the synthesis of a homologous series of bicyclic iron-amino phosphirane (**4**) and phosphirene (**5**) $Fe(CO)_4$ complexes, which were obtained by the intramolecular addition of transient phosphinidene complex [R*i*PrNP=$Fe(CO)_4$] (**3**) to unsaturated bonds (Scheme 1).[15] The in situ generation of phosphinidene complex **3** by the anionic reaction of a dichlorophosphane (**1**) with Collman's reagent (**2**)[16] is one of the few methods to gain access to these highly reactive phosphorus complexes.[17] The series shown in Scheme 2 displays a remarkable diversity in stabilities. Compounds **4d** and **5e** are crystalline, **4c** is a distillable oil, **4e** and **5d** are unstable oils, and **4b** and **5b-c** could not be isolated or observed. Given the ease of retroaddition of the simpler monocyclic phosphirane $Fe(CO)_4$ complexes,[18] the stability of **4c-d** and **5e** is surprising, but their ability to undergo retroaddition to regenerate the transient phosphinidene complex could be shown by reacting them with alkynes, thus revealing dynamic behavior. The reactivity towards phenylacetylene, giving $Fe(CO)_4$-complexed phosphirenes, differs markedly with phosphirane **4d** reacting about 30 times faster than the smaller **4c** (k_{obs} $2.9 \cdot 10^{-4}$ s^{-1} vs. $9.7 \cdot 10^{-6}$ s^{-1}) and much faster than phosphirene **5e** (k_{obs} of $5.2 \cdot 10^{-7}$ s^{-1}). Nevertheless, the formation of bicyclic **4** and **5** is surprising as *inter*molecular cycloaddition might be a viable alternative that could lead to oligomeric or polymeric materials.



Scheme 1 – Intramolecular phosphinidene addition leading to 2-aza-1-phosphabicyclo[*n*.1.0]alkanes **4** (*n*=3-5) and 2-aza-1-phosphabicyclo[*n*.1.0]alkenes **5** (*n*=4-5) at -30°C (*m*=*n*-1).

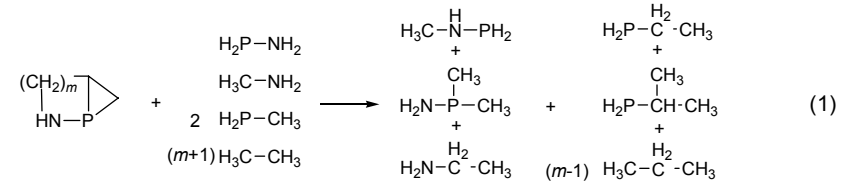


Scheme 2 - Bicyclic phosphiranes and phosphirenes. Compounds in brackets could not be isolated.

We report on the high-level ring strain energies of these 2-aza-1-phosphabicyclo-[*n*.1.0]alkanes and -alkenes (*n* = 1-5), simplified by removing the metal group and the amino substituent from **4** and **5**, which are then denoted with capital letters. The heterocyclic bicyclo[1.1.0]butane (**4A**) and -butene (**5A**) are part of this study aimed to quantify the strain effect of ring fusion on the three-membered heterocycles and to rationalize the experimentally observed stability/reactivity of **4** and **5**. Whereas ring strain reflects the energy released by breaking up the cyclic system into strain-free components, we presume that it also relates to the reactivity of bicyclic structures. Specifically, although the addition of [*i*PrNPFe(CO)$_4$] to ethylene is estimated to be exothermic by 9.4 kcal/mol, the reaction has a barrier of only 6.2 kcal/mol (BP88/TZP).[18] It is then reasonable to assume that the rate of retroaddition of **4** and **5** relates to the magnitude of their ring strain energies. A larger ring strain destabilizes the heterocycle with respect to the phosphinidene and would imply an easier release of the phosphinidene moiety.

5.2 Results and Discussion

The G3(MP2[19]) ring strain energies of the [*n*.1.0]bicyclic structures **4A-E** and **5A-E** are calculated using the homodesmotic[9] equations 1 and 2 where *m* = *n*-1. The strain energies of the corresponding hydrocarbons, the bicyclo[*n*.1.0]alkanes **6** and the bicyclo[*n*.1.0]alkenes **7**, are calculated in the same manner. Finally, for proper evaluation, we include the strain energies for the monocyclic hydrocarbons **8** and the heterocyclic rings **9** with a ring size of 3 to 7. The molecular graphs and energies are summarized in Table 1. This table also lists the excess strain energy (ESE),[14] which is the difference between the strain energy of a polycyclic compound and that of its separate composite rings, and the olefinic strain (OS),[20] which is the difference in strain energy between the unsaturated and saturated analogue. In this table is further listed the substitution strain energy (SSE), which we define as the difference in strain energy between the hetero substituted system and its hydrocarbon analogue. As expected, the calculated strain energies (SE) of **6A-E**, **7B** and **8A-E** agree well with earlier reported computational and experimental data.[21-22] The MP2(full)/6-31G* optimized structures for **4A-E**, **5A-E**, **6A-E**, and **7A-E** are shown in Table 2.



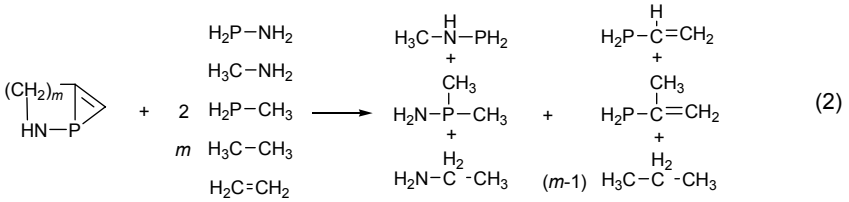
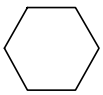
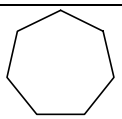
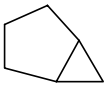
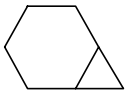
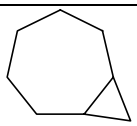
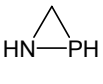
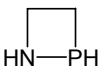
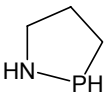
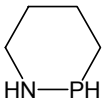
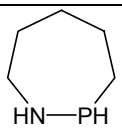
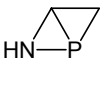
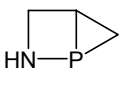
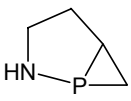
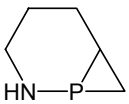
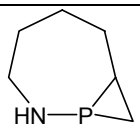
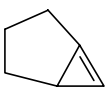
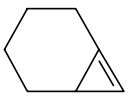
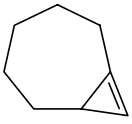
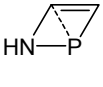
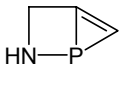
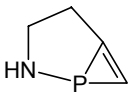
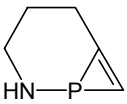
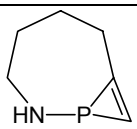
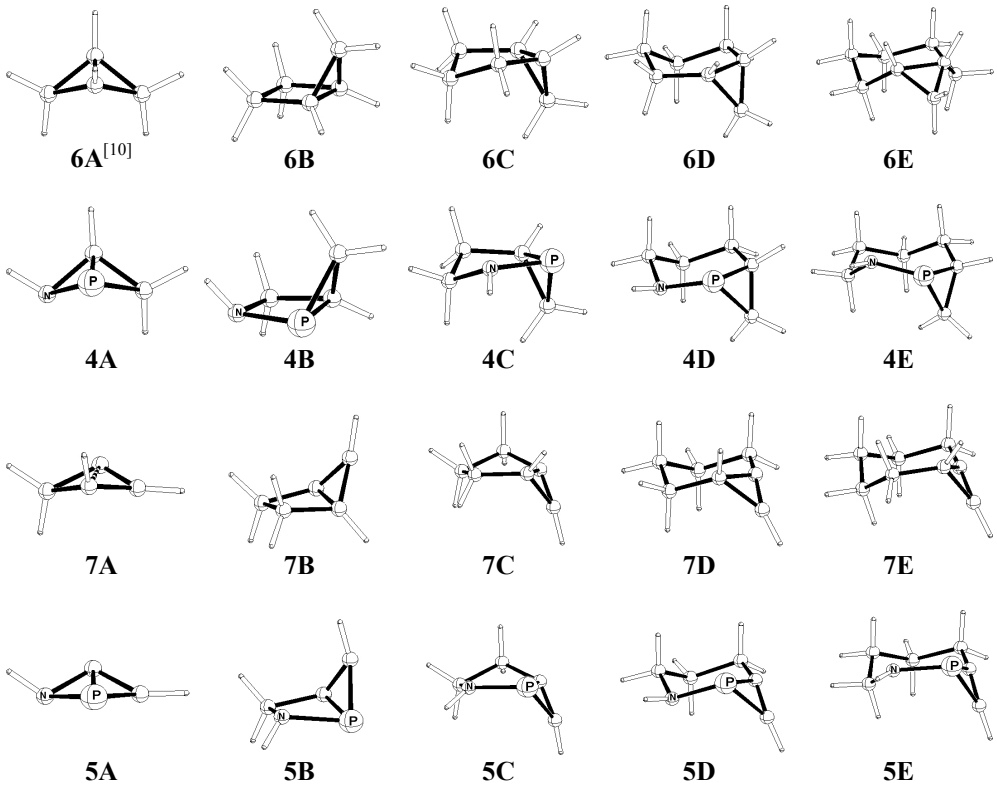


Table 1 - G3(MP2) strain energies (in kcal/mol) for bicyclo[*n*.1.0]alkanes, –alkenes and monocycles.

					
	8A	**8B**	**8C**	**8D**	**8E**
SE	28.4[b]	26.7	6.5	chair: 0.6 boat: 6.8	6.7
					
	6A	**6B**	**6C**	**6D**	**6E**
SE	68.1[c]	56.7	32.7	32.2	31.6
ESE	11.3	1.6	-2.2	3.2	-3.5
					
	9A	**9B**	**9C**	**9D**	**9E**
SE	26.5[b]	23.1	5.1	1.1	5.2
SSE	-1.9	-3.6	-1.5	0.5	-1.5
					
	4A	**4B**	**4C**	**4D**	**4E**
SE	57.7	45.5	27.0	28.0	30.8
ESE	9.8	0.9	0.6	5.5	4.2
SSE	-10.4	-11.2	-5.7	-4.2	-2.6[d]
					
	7A	**7B**	**7C**	**7D**	**7E**
SE	101.3	114.0	75.9	62.6	58.2
ESE	16.9	31.3	13.4	6.0	-4.5
OS	33.2	57.3	43.2	30.4	26.6
					
	5A	**5B**	**5C**	**5D**	**5E**
SE	92.3	91.1	58.1	46.0	39.6
ESE	26.8	29.0	14.1	6.0	-4.6
OS	34.6	45.6	31.1	18.0	8.8
SSE	-9.0	-22.9	-17.8	-16.6	-18.6

[a] ESE is excess strain energy, OS is olefinic strain, and SSE is substitution strain energy. [b] Ref. 10. [c] Ref. 11. [d] Note 23.

Table 2 - MP2(full)/6-31G* optimized structures for phosphiranes **4**, phosphirenes **5**, and their all-carbon analogues.



The influence of cyclopropanation will be discussed first for the saturated hydrocarbons by comparing the strain energies of the cycloalkanes **8** with those of the bicyclic structures **6**, followed by an evaluation of the effect of replacing a CH_2CH unit for an isovalent NHP unit in the resulting heterobicyclic structures **4**. A similar procedure will be followed in the second section to delineate the strain in the unsaturated structures **5**. These analyses will be balanced against available experimental data.

5.2.1 Saturated Bicyclic Structures

Hydrocarbons. The strain energies of the cycloalkanes **8** show the established features.[21] The chair conformation of cyclohexane **8D** is virtually strain-free (0.6 kcal/mol) and 6.8 kcal/mol more stable than the boat form. The puckered five- and seven-membered rings are equally strained by, respectively, 6.5 and 6.7 kcal/mol, and this is also the case for cyclopropane **8A** (28.4 kcal/mol) and cyclobutane **8B** (26.7 kcal/mol). Cyclopropane has more angle-strain than cyclobutane[11,24] as a result of its more strained carbon atoms,[25] but also has more σ-delocalization[26-27] and less eclipsing interactions.

Spiroannulating two rings usually increases the strain over that of the two separate rings, which is expressed in the excess strain energy (ESE). This additional strain is caused by the introduction of a second small valence angle for the spiro atom, which cannot be compensated for by rehybridization.[11] Cyclopropanating the cycloalkanes (series **6**) forces *two* atoms to have smaller valence angles, but also reduces the eclipsing interaction for the larger rings and rehybridization is still possible. As a result, only bicyclo[1.1.0]butane **6A** has a large ESE of 11.6 kcal/mol, which results from angle-strain and additional 1,3-nonbonded interactions.[14a] These effects are far less pronounced in the larger bicyclo[2.1.0]pentane (**6B**, ESE 1.6 kcal/mol). Bicyclo[3.1.0]cyclohexane (**6C**) has even a *negative* ESE of 2.2 kcal/mol, because two of the eclipsing hydrogens in the cyclopentane ring are removed upon fusion with the cyclopropane ring. This effect also underlies the negative ESE of bicyclo[5.1.0]octane **6E**. Cyclopropanating cyclohexane leads to a positive ESE of 3.2 kcal/mol (**6D**), because fusion causes the cyclohexane ring to adopt a half-boat conformation.

Heterobicyclic structures. The increase in angle strain that results on nitrogen substitution is balanced by the decrease in strain resulting upon phosphorus substitution, because this latter element is able to accommodate much smaller angles than carbon. Moreover, the number of (possibly) eclipsing hydrogens is reduced. Consequently, N,P-substitution of the cycloalkanes is seen to result in small negative substitution strain energy (SSE) values that show the 2-aza-1-phosphacycloalkanes **9** to be slightly less strained than their hydrocarbon analogues. The exception is cyclohexane for which the heterocyclic ring is slightly more strained (+0.5 kcal/mol) as a result of the adjustment of the ideal bond angles and the absence of eclipsing hydrogens in cyclohexane.

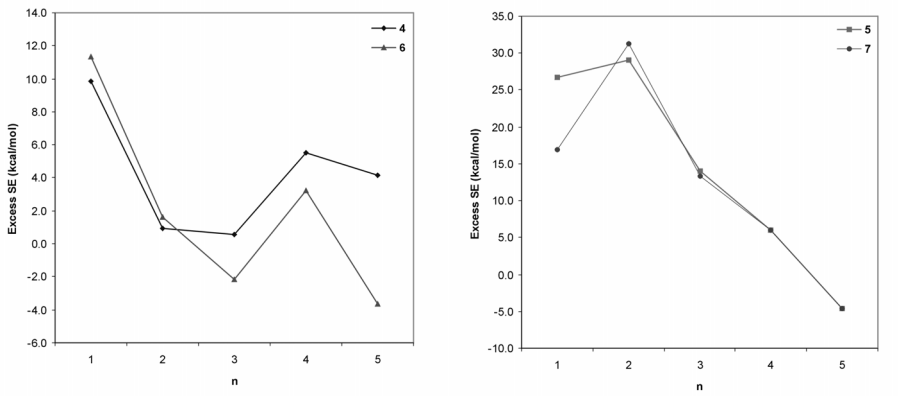


Figure 1 - (a) Excess Strain Energy (in kcal/mol) for the 2-aza-1-phosphabicyclo[*n*.1.0]alkanes (**4**) and their hydrocarbons analogues (**6**), and (b) for the 2-aza-1-phosphabicyclo[*n*.1.0]alkenes **5** and their hydrocarbon analogous **7**.

Both effects, the cyclopropanation and the N,P-substitution, are present in the 2-aza-1-phospha-bicycloalkanes **4A-E**. Figure 1a graphically displays the relationship of the excess strain energy with ring size for both bicyclic systems **4** and **6**. Electronegative elements adjacent to a three-membered ring, in the present case nitrogen, reduce the surface density and therefore diminish σ-delocalization,[11] which explains why **4C-E** have larger ESE[28] values than their hydrocarbon

analogues **6C-E**. These ESE values are for the smallest heterobicyclic rings **4A-B**, however, smaller than those for the corresponding hydrocarbons **6A-B**, because the smaller bond angles are better accommodated by the bridgehead phosphorus, which is corroborated by the smaller SSE values on increasing the ring size. This favorable influence of a bridgehead phosphorus can be illustrated by comparing bicyclo[1.1.0]butane **4A** (SE 57.7 kcal/mol) with the even more strained 2-aza-bicyclo[1.1.0]butane **10** (SE 74.9 kcal/mol, not displayed) where only the phosphorus atom is replaced for a carbon.[11] Specifically, the sizable ESE of **4A** almost doubles in **10** (9.8 vs 18.3 kcal/mol, respectively) and likewise the large negative SSE for **4A** becomes a positive one in **10** (-10.4 vs. +6.8 kcal/mol, respectively).

Thus, the least strained structure of the series is the five-membered ring containing bicyclo[3.1.0]hexane **4C** (27.0 kcal/mol), although the one carbon larger bicyclo[4.1.0]heptane **4D** is only 1.0 kcal/mol more strained despite its larger ESE (Δ 4.9 kcal/mol), while the difference with bicyclo[4.1.0]octane **4E** is more (ΔSE 3.8 kcal/mol). Interestingly, the ESE for this structure is a 7.7 kcal/mol larger than that for hydrocarbon **6E**. The opposite trend in strain energies is seen for the corresponding hydrocarbons of which the largest one (**6E**) is the least strained. Thus, N,P-substitution reverses the ring strain order of the hydrocarbons from **6C** > **6D** > **6E** to **4C** < **4D** < **4E** for the heterobicyclic structures.

Comparison with experimental data. The calculated SE values of bicyclic phosphiranes **4B-E** correlate exceptionally well with the reported experimental data[15] for phosphiranes **4**. The most strained heterocyclic compound **4b** could indeed not be synthesized and that of **4a** was not even attempted. Both larger bicyclic systems **4c** and **4d** have been isolated as stable compounds, being apparently the least strained ones, which is in accordance with the calculations on the simpler models. The difference in reaction rates of these systems concurs with the calculation of the 2-aza-1-phosphabicyclo[4.1.0]hexane frame (**4c**) as the least strained one of the two, as the larger bicyclo[4.1.0]heptane **4d** reacts 30 times faster with phenylacetylene than bicyclo[3.1.0]hexane **4c** does. The slightly more strained **4e** (SE = 30.8 kcal/mol) has been isolated, but does not survive purification procedures. Apparently, this molecule is more strained, which again is in accordance with the calculated strain energies.

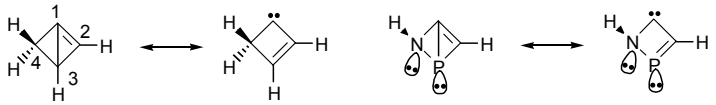
5.2.2 Unsaturated Bicyclic Structures

This section starts again with an evaluation of the hydrocarbons before discussing the N,P-containing unsaturated bicyclic structures.

Hydrocarbons. Fusion of a cycloalkane with a cyclopropene instead of a cyclopropane ring is expected to introduce considerably more strain and this is confirmed by the calculated strain energies, excess strain energies[29] and olefinic strains of the bicyclo[*n*.1.0]alkenes **7** (*n* = 1-5) that are listed in Table 1. This, of course, is due to the unsaturated bridgehead carbon that has 'inverted' sp^2 character[30] with limited rehybridization options.

The smallest member of the series, bicyclo[1.1.0]butene **7A**, has an expectedly large strain energy of 101.3 kcal/mol, which is nevertheless a surprisingly 12.7 kcal/mol less than that for the larger bicyclo[2.1.0]pentene **7B**. This difference is even more pronounced in the olefinic strain, which is for

7A much smaller than that for **7B** (33.2 vs 57.3 kcal/mol) and more comparable to that of the parent three-membered cyclopropene (27.6 kcal/mol). Bicyclo[1.1.0]butene is clearly stabilized, which is also reflected by the short C2-C3 bond (1.436 Å), the elongated C1-C3 distance (1.788 Å), and the large puckering angle (145°) for the bicyclic frame, all of which point to a strong contribution of the vinyl carbene mesomeric form (see Scheme 3a). This stabilization reflects the established electron delocalization that underlies the relationship between cyclopropenes and vinyl carbenes.[31]



7A **5A**

Scheme 3 – Resonance stabilization of (a) bicyclo[1.1.0]butene **7A** and (b) heterobicyclic **5A**.

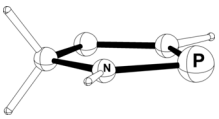
Bicyclo[2.1.0]pentene **7B**, is a more conventional bicyclic structure with normal C=C (1.324 Å) and transannular C-C bond lengths (1.502 Å). Yet, the olefinic bridgehead carbon is significantly pyramidalized (Σ angles 292.0°) and the olefinic bond is therefore twisted, which is the origin of the large olefinic strain (57.3 kcal/mol). The next larger member of the series, bicyclo[3.1.0]hexene **7C**, is expected to be less strained, and this is indeed the case (SE 75.9 kcal/mol), even though the olefinic strain (43.2 kcal/mol) remains substantially larger than for cyclopropene. On further enlarging the aliphatic ring the strain reduces still more but to a smaller degree as illustrated by the OS value, which is for bicyclo[4.1.0]heptene **7D** (SE 62.6 kcal/mol) only 2.8 kcal/mol more than for cyclopropene (27.6 kcal/mol) and even 1.0 kcal/mol less for bicyclo[5.1.0]octene (SE 58.2 kcal/mol). These data comply with experimental data in the literature that report compound **7d** to react already at –90°C, whereas **7e** is persistent for several hours at room-temperature.[32] In summary, the strain of the bicyclo[*n*.1.0]alkenes relates to the olefin strain and thus to the pyramidalization of the bridgehead olefinic carbon, which is linked to the olefinic angle of the larger ring (Table 3).

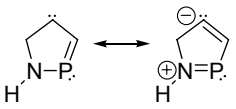
Table 3 - Strain energies (kcal/mol) and bond-angles (°) around the bridge-head olefinic carbon (e.g. *L* C3-C1-C4, sch. 3a)

	n	**7**				**5**			
Cmpd	ring	SE	OS	Σ angles	angle	SE	OS	Σ angles	angle
A	1	101.3	33.2	200.3	52.2	92.3	34.6	217.7	58.2
B	2	114.0	57.3	292.0	95.2	91.1	45.6	291.4	96.2
C	3	75.9	43.2	320.9	114.5	58.1	31.1	327.4	115.6
D	4	62.6	30.4	347.4	129.2	46.0	18.0	346.2	131.4
E	5	58.2	26.6	357.0	139.8	39.6	8.8	356.9	141.7
cyclopropene		56.0	27.6	360.0	150.0	39.0	17.6	360.0	146[33]

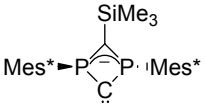
Heterobicyclic structures. With the bridgehead phosphorus and its neighboring nitrogen present in the bicyclic frame, as in **5**, the strain for each member is less than that of the all hydrocarbon homologue (**7**), as expected (see above), but the excess strain energies (ESE) are remarkably similar for both systems (Table 1), as graphically displayed in Figure 1b. This strongly suggests that bond-angle strain is also the determining factor for the heterobicyclic structures and hence the olefinic strain, and thus the pyramidalization of the olefin carbon (Table 3). We discuss specific aspects.

The smallest member, 2-aza-1-phospha-bicyclo-[1.1.0]butene **5A** (n = 1), is deformed, like **7A**, to reduce its otherwise excessive strain energy. Electron delocalization is evident from the elongated C=C (1.421 vs ca. 1.31 Å for **5C-E**) and transannular C-P bonds (2.088 vs 1.82 Å for **5C-E**), and the shortened peripheral C-P bond (1.804 Å) that suggests double bond character. These features are indicative of the mesomeric contribution of carbene phospha-alkene form (Scheme 3b). Compared to the OS of 1*H*-phosphirene (17.6 kcal/mol),[10] that of **5A** is large (34.6 kcal/mol), yet much smaller than that of the larger bicyclic phosphirene **5B** (45.6 kcal/mol), which underscores the stabilization that results from electron delocalization. Whereas these structures have similar strain energies, bicyclic phosphirene **5B** (SE 91.1 kcal/mol) is more condensed than **5A** (SE 92.3 kcal/mol) as a result of the stronger interaction between the phosphorus atom and the pyramidal bridge-head olefinic carbon (1.791 Å). Because of its condensed nature, bicyclo[2.1.0]pentene **5B** gains the most by N,P-substitution (SSE -22.9 kcal/mol) of the series. Yet, also the high strain in this structure can be released in part, like **4A**, by cleaving the relative weak P-C bond (2.672 Å) to give the 23.2 kcal/mol more stable planar isomer **5B'** (SE 67.9 kcal/mol), thereby indicating that the bicyclic structure is not likely to be observed experimentally. Resonance stabilization of **5B'** is suggested by the elongated C=C bond (1.394 Å), the shortened P-C bond (1.751 Å), and the planar nitrogen (see Figure 2a). Structure **5B'** is then best described as a hybrid of a phospha-alkene carbene and a mesomeric azaphosphole carbene that shows similarities with the recently developed carbenes by Bertrand[4] and Niecke's 1,3-diphosphacyclobutane-2,4-diyl-2-ylidenide **11**.[1c] A similar planar structure for **5A** is not feasible and represents, in fact, the transition (E_a = 11.9 kcal/mol) for inversion of the puckered form.





5B'



11

Figure 2 - Planar isomer **5B'** of 2-aza-1-phosphabicyclo[1.1.0]butene and **11**.

Enlarging the cycloalkane ring reduces its bridgehead CCP-angle and consequently the strain energy (Table 3). 2-Aza-1-phospha-bicyclo[1.1.0]hexene **5C** is a large 33.0 kcal/mol less strained than **5B** and even 12.1 kcal/mol more for the next larger homologue **5D** that has a phosphirene fused to a six-membered ring. The SE for the next larger bicyclic **5E** is still further reduced (by 6.4 kcal/mol) to become virtually the same as 1*H*-phosphirene itself.[11] This significant decrease in SE for this series of structures **5C** > **5D** > **5E** contrast that of the saturated series **4C** < **4D** < **4E** and reflects the

energetic cost of 'inverting' an sp^2 hybridized carbon or in other words twisting an olefinic carbon (Table 3). This behavior mimics that of the all-hydrocarbon series **7** as underlined by the similar N,P-substitution effect (SSE values, Table 1).

Comparison with experimental data. The calculated ring strain energies of the bicyclic phosphirenes **5C-E** are in excellent agreement with the reported experimental data. Assuming that high SE values reduce the structural accessibility and viability, it is clear why the smallest phosphirene complexes **5b-c** could not be synthesized. It is equally clear that of the two compounds that could be obtained, **5e** is more stable than **5d** and indeed the latter could not be obtained in pure form. That **5e** reacts slowly with phenylacetylene is also in line with expectations, considering that **5E** is more strained than 1*H*-phosphirene, indicating a slight preference for intermolecular cycloaddition.

5.3 Conclusion

G3(MP2) calculations show the ring strain energies (SE) of the bicyclo[*n*.1.0]alkanes (**6**) with *n* = 2-5 to be similar to that of the sum of the separate rings and this is also the case on replacing $CHCH_2$ for the isovalent PNH unit (**4**). Of course, the heterobicyclic structures are strained less than the hydrocarbons, as reflected in negative substituent strain energy (SSE) values, which become smaller on enlarging one of the rings. The bridgehead phosphorus atom accommodates small valence angles better than carbon, which is quite evident in the much more strained bicyclo[1.1.0]butanes **4A** and **6A**.

The strain energies for the unsaturated series of bicyclo[*n*.1.0]alkenes are larger than the sum of the separate rings, both for the hydrocarbons **7** and the heterocyclic structures **5** except for the largest member with *n* = 5. On enlarging one of the rings the strain energy decreases monotonically. The smaller members are extremely strained as a result of the 'inverted' nature of the bridgehead carbon that causes twisting of the C=C bond. For both bicyclo[1.1.0]butene structures **7A** and **5A** this brings about a weakening of the transannular bond to enable stabilization by a vinyl carbene resonance structure. This also occurs in the dihetero analogue of bicyclo[2.1.0]pentene (**5B**) to give a 23 kcal/mol more favorable monocyclic form that is likewise stabilized by a vinyl carbene resonance form.

The calculated strain energies for the model 1-aza-1-phospha-bicyclo[*n*.1.0]alkanes and –alkenes correlated exceptionally well with the reported experimental data on the $Fe(CO)_4$ complexed derivates, not only with respect to the isolated compounds but also with respect to their observed reactivities.

5.4 Computational details

All calculations were performed using the GAUSSIAN 98 suite of programs.[34] Structures were optimized with density functional theory using Becke's three-parameter hybrid exchange functional[35] and the Lee *et al.* correlation functional[36] (B3LYP) and verified as minima by frequency calculations. All strain energies were determined by calculating the G3(MP2)[19] enthalpy at 298.15 K for the homodesmotic reaction[9] involving the ring structure. Structural parameters of the calculated compounds refer to geometries optimized at the MP2(full)/6-31G(d) level, generated as part of the G3(MP2) calculation.

Acknowledgements

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Supporting Information

Supporting information containing the calculated energies and *xyz*-coordinates of the species discussed is available from the author.

5.5 Notes and References

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Chapter 6

Phosphepines: Convenient Access to Phosphinidene Complexes

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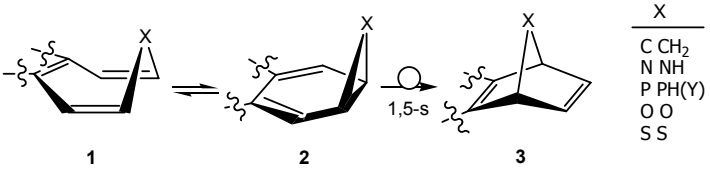
J. Am. Chem. Soc. **2005**, *127*, 5800-5801

6.1 Introduction

The cycloheptatriene – norcaradiene (CHT-NCD) equilibrium exemplifies a 6-el electrocyclic reaction with a modest barrier separating the valence tautomers **1C** and **2C**.[1] Less is known about the heterocyclic analogues (X = O, S, NR, PR). For those with an oxygen atom, benzene oxide **2O** is the more stable form, but entropy factors shift the equilibrium toward oxepin **1O** at room temperature.[2] Only the monocyclic form is observed for thiepins[3] **1S** and 1*H*-azepines[4] **1N** and both require bulky groups and/or extended conjugation for stability. Of the phosphorus analogue, phosphepine **1P**, only its oxide[5] and 2,7-dialkyl-substituted[6] and annelated[7-8] derivatives are known, but without

structural details. Here we describe a computational analysis of the **1P**-**2P** equilibrium and present new stable phosphepine derivatives and a novel application.



Scheme 1 – Valence isomers of cycloheptatriene.

6.2. Results and Discussion

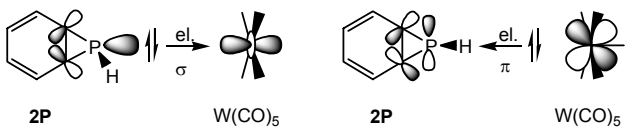
Phosphepines equilibrate with phosphanorcaradienes (benzene phosphines), such as CHT with NCD. DFT calculations for the parent system give an energetic preference for NCD **2P** over CHT **1P** ($\Delta E_{2\text{-}1}$ –4.2 kcal/mol, Table 1) with a modest **1P**→**2P** barrier (10.6 kcal/mol), reflecting the same behavior as the thia analogues ($\Delta E_{2\text{-}1}$ –7.8 (**S**) kcal/mol). A 1,5-sigmatropic shift relates NCD **2P** with the 15.5 kcal/mol less stable 7-phosphanorbornadiene **3P**, neither of which is known experimentally, except for a strained derivative of **3P**,[9] presumably due to release of the phosphorus group to give pentamers, $(PR)_5$.

Table 1 - B86-P88/TZP relative energies (in kcal/mol) for **1P**, **2P**, **3P**,and their $W(CO)_5$ and benzannelated derivatives.[a]

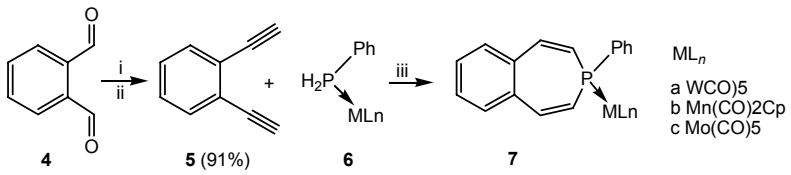
R(Y)	1P	2P	3P
H	0.0	–4.2	11.3
$H(W(CO)_5)$	0.0	1.5	7.8
H + benzo[b]	0.0	11.0	4.2
$H(W(CO)_5)$ + benzo-[b]	0.0	16.8	1.3

[a] The lone pair and $W(CO)_5$ group occupy the axial (**1**) or syn (**2**, **3**) position.[10] [b] Benzannelation as indicated in Scheme 1.

Transition metal coordination at phosphorus stabilizes **1P** over **2P** because the distal C–C bond is weakened by σ,π-interactions (Scheme 2), reversing the order for $W(CO)_5$ (($\Delta E_{2\text{-}1}$ 1.5 kcal/mol). Due to extended conjugation benzannelation has an even stronger influence, reversing the CHT-NCD equilibrium in favor of **1P** by 11.0 kcal/mol. These cumulative electronic effects give a 16.8 kcal/mol energetic preference of benzophosphepine $W(CO)_5$ complex over its valence isomer **2P** with a 24.7 kcal/mol barrier for electrocyclization. These effects stabilize 7-phosphanorbornadiene **3** even more, reducing the energy difference with the phosphepine complex to 1.3 kcal/mol.



Scheme 2 - HOMO LUMO interactions between **2P** and $W(CO)_5$.



Scheme 3 - Synthesis of benzophosphine complex **7**. i) CBr_4, PPh_3; ii) LDA; iii) KOH, THF, at 25°C.

On the basis of these calculations benzophosphepine complexes **7** are expected to be stable at room temperature. Indeed, **7** could be synthesized from the complexed phosphine and 1,2-diethynylbenzene (**5**) by a modified Märkl's procedure[7] (Scheme 3). Dialkyne **5** was obtained in 91% yield from commercially available *o*-phthaldialdehyde (**4**) by a one carbon homologation-oxidation sequence. The base-promoted double hydrophosphination of **5** with PH_2Ph-$W(CO)_5$ (**6a**) gave 3*H*-3-benzophosphepine-$W(CO)_5$ **7a** in 74% yield as yellow crystals. $W(CO)_5$ coordination causes shielding of the ^{31}P NMR resonance (δ −15 vs −33 ppm), shielding of the C1, C5 ^{13}C NMR resonances (by 6 ppm), and reduces the $^2J_{CP}$ coupling constants (1.6 vs 21.1 Hz).[7] Distinctive are the coupling constants for the olefinic protons with a sizable $^3J_{HH}$ (12.4 Hz) and with a $^3J_{HP}$ (33.4 Hz) being much larger than the $^2J_{HP}$ (21.3 Hz).

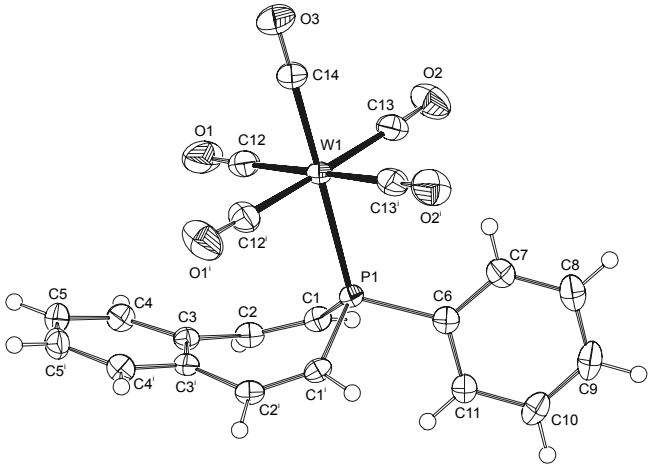


Figure 1 – Displacement ellipsoid plot (50% probability level) of 3-phenyl-3*H*-benzophosphepine-$W(CO)_5$. Selected bond distances (Å), angles (deg) and torsion angles (deg): W1-P1 2.5279(9), W1-C12 2.053(3), C1-C1i 2.792, P-C1 1.814(2), C1-C2 1.337(3), C2-C3 1.479(3), C3-C3i 1.417(3), C3-C4 1.408(3), C4-C5 1.395(4), C5-C5i 1.385(4), C1-P-C1i 100.64 (11), W-P-C6-C7 0.00, C3-C2-C1-P 0.6(4), C1-C2-C3-C4 146.0(3).

The crystal structure (*Cs*-symmetry) shows alternating C=C bonds (no homoaromaticity) for the boat-shaped phosphepine ring (Figure 1) that has the phosphorus atom shifted out of the hydrocarbon plane by 67.20(13)°. The orthogonal phenyl group is on the mirror plane and bisects the C1-P-C1i angle. The P-C1(C1i) bonds are very short (1.814(3) Å).

Because the phosphorus group is introduced in the final step, the synthesis allows for versatility in substituents and metal complexes. Illustrative is the condensation of **5** with $PhPH_2$-$Mn(CO)_2Cp$ that gives manganese complexed phosphepine **7b** (35%). The molecule in the crystal shows again *Cs*-symmetry, but has a flatter phosphepine ring with a dihedral angle of 34.49(8)° between the C1-P1-C1i and hydrocarbon planes (Figure 2). This is best explained by a steric effect of the Cp, hanging over the phosphepine ring, in which C=C bond alternation is again evident. The orthogonal phenyl group bisects the C1-P-C1i angle and the Mn-P bond has a normal distance of 2.1954(5) Å.[11] The more shielded ^{31}P NMR resonance at +64 ppm points to less electrophilic character for the phosphorus group than in **7a**; the ^{1}H and ^{13}C NMR parameters are similar including the $^{2}J_{HP}$ (20.7 Hz) and $^{3}J_{HP}$ (32.1 Hz) coupling constants.

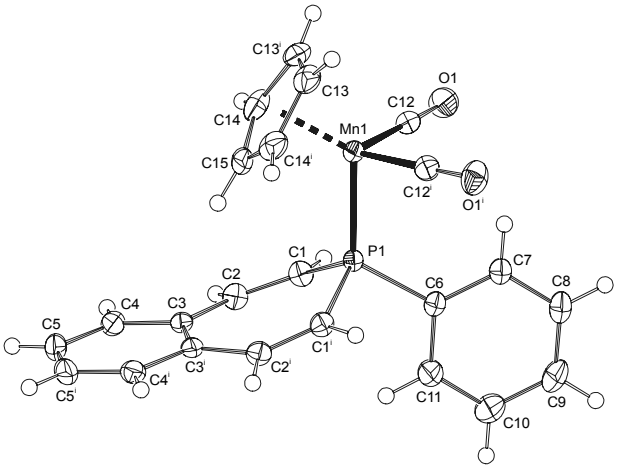


Figure 2 – Displacement ellipsoid plot (50% probability level) of 3-phenyl-3H-benzophosphepine-Mn(CO)2Cp. Selected bond distances (Å), angles (deg) and torsion angles (deg): Mn-P 2.1954(5), P-C1 1.79855(14), P-C6 1.8345(18), Mn-C12 1.7749 (14), C12-O1 1.1588(18), C1-C2 1.3327(19), C1-P-C1' 105.18(7), Mn-P-C1 114.44(5), C12-Mn-P-C6 46.34 (5), P-C1-C2-C3 –3.4(3).

Phosphepines **8** and **9** are known to decompose readily to the aromatic hydrocarbon and $(RP)_5$, presumably by expelling [RP] from the NCD intermediates.[7-8] Interestingly, in the case of complex **7** this would result in the expulsion of a transition metal stabilized phosphinidene [$RP{=}ML_n$]. Extremely few synthetic routes enable access to such phosphinidene complexes,[12] especially those with electrophilic properties. In fact, cheletropic elimination from complexed 7-phosphanorbornadienes **10** is the only general route to generate [$R\text{-}P{=}M(CO)_5$],[23a] but its synthesis is longer, less flexible to metal variation, and requires for milder conditions a catalyst that can alter the course of the reaction.[13] Nevertheless, *in situ* trapping of the transient species has led to a plethora of useful organophosphorus compounds.[14]

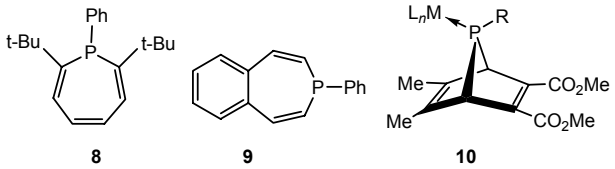
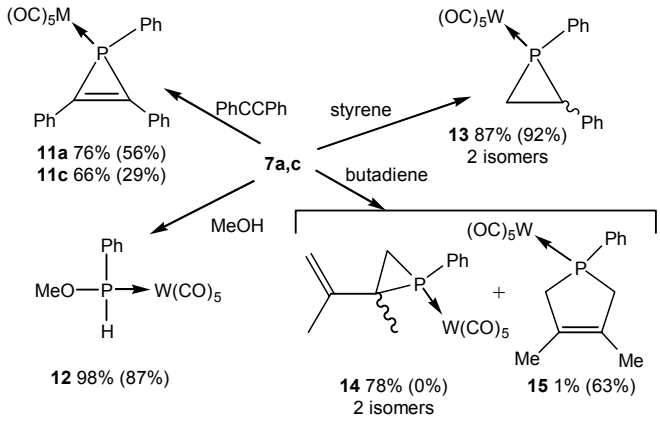


Chart 1 - Stabilized phosphepines and phosphinidene precursor **10**.

Benzophosphepine **7a** reacts with the test set of molecules, first used for the reaction with **10**, to give at 75-80°C the same addition/insertion products,[12a,15-16] but in better yields (Scheme 4) and requiring only removal of solvent and naphthalene (by sublimation). The 30°C advantage in reaction temperature is evident from the formation of vinylphosphirane **14** from 2,3-dimethylbutadiene, whereas phospholene **15** is the main product with **10a**[12a] due to a 1,3-sigmatropic shift that occurs above 80°C.[15] Reaction of molybdenum complex **7c**, obtained from **5** and $PhPH_2$-$Mo(CO)_5$ (67%), with tolan gives phosphirene **11c** in 66% yield versus 29% with **10c**.[16] Access to unprecedented far less electrophilic phosphinidenes is illustrated by the reaction of manganese complex **7b** with phenylacetylene that results in a $Mn(CO)_2Cp$ complexed phosphirene (81%, ^{31}P NMR δ –59.0), suggesting the intermediacy of the novel phosphinidene [R-P=$Mn(CO)_2Cp$].



Scheme 4 - Phosphinidene reactions of **7** (and **10**).

6.3 Conclusion

In conclusion, we presented a very short synthesis to diverse stable 3*H*-3-benzophosphepine complexes that are excellent precursors to electrophilic phosphinidene complexes, requiring very mild reaction conditions and an extremely simple workup.

6.4 Experimental part

Calculations

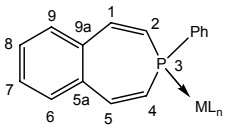
All geometry optimizations were performed with the ADF[17] program, using a triple ζ basis set with polarization functions, the local density approximation (LDA) in the Vosko-Wilk-Nusair parameterization[18] with nonlocal corrections for exchange (Becke88)[19] and correlation (Perdew86)[20] included in a selfconsistent manner, and the analytical gradient method of Versluis and Ziegler.[21] Minima were confirmed to have only positive force constant and the transition structure to have only one imaginary value using the Gaussian98 program package,[22] using geometries optimized with the BP86 exchange-correlation potentials and the LANL2DZ basis set for tungsten and 6-31G(d) for all other elements.

Synthesis

All experiments were performed under an atmosphere of dry nitrogen. All solvents were distilled from LiAlH4 (pentane, diethylether), sodium benzophenone (THF) or P_2O_5 (dichloromethane) before use. Diisopropylamine was distilled from KOH. Phosphane complexes 6a-b were synthesized according to literature procedures.[23] Tetrabromomethane was sublimed before use. All other compounds were purchased and used as such. The NMR-data of 1,2-diethynylbenzene[24], phosphirenes 11[12a,25] phosphinite complex 12[26] and phosphiranes 13-14[27] compare well with literature data. NMR spectra were recorded on a Bruker WM 250 (^{1}H, ^{13}C, ^{31}P) and Bruker MSL 400 (^{1}H, ^{13}C), IR spectra on a Mattson-6030 Galaxy spectrometer and high-resolution mass spectra (HR-MS) on a Finnigan MAT 900 spectrometer. NMR-chemical shifts are internally referenced to the solvent for ^{1}H ($CDCl_3$: 7.25 ppm) and ^{13}C ($CDCl_3$: 77.0 ppm) and externally for ^{31}P to 85% H_3PO_4.

1,2-diethynylbenzene (5): Triphenylphosphine (27.52 g, 104.9 mmol) was added portion-wise to a cold (0°C) solution of tetrabromomethane (17.39 g, 52.4 mmol) in 250 mL dichloromethane. The resulting orange-red solution was stirred at room-temperature for 20 min. After cooling to 0°C a solution of 3.07 g (22.8 mmol) *o*-phtaldialdehyde in 100 mL dichloromethane was added slowly and the mixture was stirred in the dark at room-temperature for 2hrs. The reaction mixture was extracted with distilled water (2x100 mL) and the water-layers washed with dichloromethane (2x50mL). The combined organic layers were dried ($MgSO_4$) and concentrated. Pentane (7x150 mL) was added and the resulting suspension was decanted after stirring. After addition of another 150 mL of pentane to the suspension it was filtered and all pentane fractions were combined, concentrated and purified by column chromatography (SiO_2, 1% Et_2O in pentane, R_f=0.5), yielding a yellow oil (9.85 g, 22.1 mmol, 97%). ^{13}C NMR ($CDCl_3$): δ 135.4 (CH=), 134.58 (*ipso*-ArC), 128.8 (*o*-ArC), 128.4 (*m*-ArC), 93.1 (=CBr_2). ^{1}H NMR ($CDCl_3$): δ 7.47-7.56 (m, 2H, *o*-ArH), 7.42 (s, 2H, CH=), 7.35-7.39 (m, 2H, *m*-ArH). IR (KBr): ν (cm^{-1}): 808 (m), 858 (m), 951 (m), 1186 (m), 1269 (m), 1460 (m), 1599 (m), 1796 (s). HRMS: Calcd for $C_{10}H_6{}^{79}Br_2{}^{81}Br_2$: 445.71620. Found: 445.71701. M/*z* (%): 446 (5, $[M]^+$), 367 (20, $[M-{}^{79}Br]^+$), 365 (20, $[M-{}^{81}Br]^+$), 286 (100, $[M-{}^{81}Br-{}^{79}Br]^+$), 126 (38, $[M-Br_4]^+$).
48.8 mL (78.1 mmol) *n*-BuLi (1.6 M in hexanes) was added to a cold (-78°C) solution of 10.3 mL (78.1 mmol) diisopropylamine in 250 mL THF. After warming up to room-temperature the solution was added carefully to a cold (-78°C) well-stirred solution of 5.82 g (13.0 mmol) **7** in 50 mL THF. After 20 min. stirring at -78°C the reaction was quenched with 130 mL sat. $(NH_4)_2SO_4$ aq. and stirred for 2hrs at room-temperature. The reaction mixture was poured out in 200 mL pentane, the organic layer was separated and washed with water, dried ($MgSO_4$), concentrated and purified using column chromatography (SiO_2, 1% Et_2O in pentane, R_f=0.42), yielding a colorless liquid (1.54 g, 12.2 mmol, 94%). ^{1}H NMR ($CDCl_3$): δ 7.48-7.54 (m, 2H, *o*-ArH), 7.27-7.34 (m, 2H, *m*-ArH), 3.33 (s, 2H, CH).

General synthesis for benzophosphepines 7: A THF solution (11.75 mL) of **5** (164 mg, 1.3 mmol) and phosphine complex **6** (1.0 mmol) was stirred overnight. Freshly ground KOH (40 mg, 0.72 mmol) was added and after 30 min, the mixture was filtered over silica and concentrated. Crystals were grown from Et_2O. Additional yield after chromatography (SiO_2, 1:4=toluene:pentane).



7a: 74%. Mp (decomp): 115 °C. ^{31}P NMR ($CDCl_3$): δ -14.8 ($^1J_{PW}$ = 237.7 Hz). ^{13}C NMR ($CDCl_3$): δ 199.6 (d, $^2J_{CP}$ = 20.6 Hz, CO_{ax}), 196.4 (d, $^2J_{CP}$ = 7.0 Hz, CO_{eq}), 140.6 (d, $^2J_{CP}$ = 1.6 Hz, C1, C5), 136.4 (d, $^3J_{CP}$ = 4.7 Hz, C5a, C9a), 135.5 (d, $^1J_{CP}$ = 46.3 Hz, *ipso*-C), 132.7 (s, C6, C9), 132.2 (d, $^2J_{CP}$ = 12.2 Hz, *o*-ArC), 130.2 (d, $^4J_{CP}$ = 2.1 Hz, *p*-ArC), 128.6 (d, $^3J_{CP}$ = 10.0 Hz, *m*-ArC), 128.1 (s, C7, C8), 127.6 (d, $^1J_{CP}$ = 36.3 Hz, C2, C4). ^{1}H NMR ($CDCl_3$): δ 7.66 - 7.74 (m, 2H, *o*-ArH); 7.37 – 7.46 (m, 3H, *m*+*p*-ArH), 7.31 (s, 4H, H6-H9), 7.13 (dd, $^3J_{HP}$ = 33.4 Hz, $^3J_{HH}$ = 12.4 Hz, 2H, H1+H5), 6.12 (dd, $^2J_{HP}$ = 21.3 Hz, $^3J_{HH}$ = 12.4 Hz, 2H, H2+H4). IR (KBr): ν (cm^{-1}), CO: 2069.7 (s), 1927.7 (s). HRMS: Calcd for $C_{21}H_{13}WPO_5$: 560.00104. Found 560.00179.

7b: Chromatography (35% CH_2Cl_2 in pentane), crystallization from toluene/pentane (35%). M.p. >114°C (decomp.). ^{31}P NMR ($CDCl_3$): δ 64.0. ^{13}C NMR ($CDCl_3$): δ 231.09 (d, $^2J_{CP}$ = 24.2 Hz, CO), 138.55 (d, $^2J_{CP}$ = 4.2 Hz, C1, C5), 136.94 (d, $^3J_{CP}$ = 3.9 Hz, C5a, C9a), 135.79 (s, *ipso*-C), 132.71 (d, $^4J_{CP}$ = 0.6 Hz, C6, C9), 132.28 (d, $^2J_{CP}$ = 10.8 Hz, *o*-ArC), 129.50 (d, $^1J_{CP}$ = 36.2 Hz, C2, C4), 129.34 (d, $^4J_{CP}$ = 2.2 Hz, *p*-ArC), 127.98 (d, $^3J_{CP}$ = 9.5 Hz, *m*-ArC), 127.82 (s, C7, C8), 81.80 (s, Cp). ^1H NMR ($CDCl_3$): δ 7.68-7.72 (m, 2H, *o*-ArH), 7.27-7.34 (m, 3H, *m*+*p*-ArH), 7.25 (s, 4H, H6-H9), 7.00 (dd, $^3J_{HP}$ = 32.1 Hz, $^3J_{HH}$ = 12.8 Hz, 2H, H1+H5), 5.96 (dd, $^2J_{HP}$ = 20.7 Hz, $^3J_{HH}$ = 12.7 Hz, 2H, H2+H4), 4.36 (d, $^2J_{HP}$ = 1.9 Hz, 5H, Cp). IR (KBr): ν = 1921.9 (s), 1849.6 (s) (CO) cm^{-1}. HRMS: Calcd for $C_{23}H_{18}MnPO_2$, 412.0425. Found: 412.0423. *M/z* (%): 412 (10) [M^+], 356 (24) [M^+-2CO], 228 (60) [M^+-2CO-$C_{10}H_8$], 128 (100) [$C_{10}H_8^+$].

7c: 67%. Mp (decomp): 106 °C. ^{31}P NMR ($CDCl_3$): δ 5.8. ^{13}C NMR ($CDCl_3$): δ 210.2 (d, $^2J_{CP}$ = 22.0 Hz, CO_{ax}), 205.2 (d, $^2J_{CP}$ = 9.1 Hz, CO_{eq}), 139.9 (d, $^2J_{CP}$ = 0.8 Hz, C1, C5), 136.6 (d, $^3J_{CP}$ = 4.8 Hz, C5a, C9a), 135.2 (d, 133.69, $^1J_{CP}$ = 48.2 Hz, *ipso*-ArC), 132.6 (d, $^4J_{CP}$ = 0.8 Hz, C6, C9), 132.3 (d, $^2J_{CP}$ = 12.8 Hz, *o*-ArC), 130.1 (d, $^4J_{CP}$ = 2.1 Hz, *p*-ArC), 128.6 (d, $^3J_{CP}$ = 9.7 Hz, *m*-ArC), 128.0 (s, C7, C8), 127.9 (d, $^1J_{CP}$ = 30.6 Hz, C2, C4.) ^1H NMR ($CDCl_3$): δ 7.70-7.79 (m, 2H, *o*-ArH), 7.42-7.45 (m, 3H, *m*+*p*-ArH), 7.30 (s, 4H, H6-H9), 7.12 (dd, $^3J_{HP}$ = 32.6 Hz, $^3J_{HH}$ = 12.8 Hz, 2H, H1+H5), 6.06 (dd, $^2J_{HP}$=20.3 Hz, $^3J_{HH}$=12.8 Hz, 2H, H2+H4). IR (KBr): ν = 2070.5 (s), 1948.1 (broad, s) (CO) cm^{-1}. HRMS: Calcd for $C_{21}H_{13}MoPO_5$: 473.9555. Found 473.9558. *M/z* (%): 474 (20) [M^+], 390 (60) [M^+-3CO], 334 (100) [M^+-5CO], 128 (95) [$C_{10}H_8^+$].

Phosphinidene reactions: Benzophosphepine complex **7** and the substrate were dissolved in toluene and placed in an oil bath (75°C) for 17hrs unless otherwise noted. Work-up included solvent evaporation, removal of naphthalene (and excess substrate) at 50°C and 1-2 mm Hg.

11a: 1.5 eq of diphenylacetylene, 9hrs at 80°C. Sublimation of diphenylacetylene at 85°C/1-2 mm Hg. Crystallization from pentane. Yellow crystals, 76%. ^{31}P NMR ($CDCl_3$): δ -159.4 ($^1J_{PW}$=268.3 Hz). ^{13}C NMR ($CDCl_3$): δ 197.7 (d, $^2J_{CP}$=31.0 Hz, CO_{ax}), 195.9 (d, $^2J_{CP}$=8.5 Hz, CO_{eq}), 137.5 (d, $^1J_{CP}$=6.3 Hz, *ipso*-ArP), 131.3 (d, $^2J_{CP}$=15.8 Hz, *o*-ArP), 130.7 (s, *p*-ArC), 130.5 (d, $^4J_{CP}$=2.5 Hz, *p*-ArP), 130.4 (d, $^3J_{CP}$=5.4 Hz, *o*-ArC), 129.3 (d, $^4J_{CP}$=0.8 Hz, *m*-ArC), 128.6 (d, $^3J_{CP}$=10.5 Hz, *m*-ArP), 128.3 (d, $^1J_{CP}$=9.5 Hz, C=), 127.2 (d, $^2J_{CP}$=6.8 Hz, *ipso*-ArC). ^1H NMR ($CDCl_3$): δ 7.88-7.91 (m, 4H, ArH), 7.45-7.60 (m, 8H, ArH), 7.30-7.40 (m, 3H, ArH).

11c: 1.5 eq. of diphenylacetylene, 21hrs at 80°C,. Light yellow crystals, 66%. ^{31}P NMR ($CDCl_3$): δ -137.9.. ^1H NMR ($CDCl_3$): δ 7.88-7.92 (m, 4H, ArH), 7.45-7.58 (m, 8H, ArH), 7.27-7.35 (m, 3H, ArH).

12: 15 eq. methanol, 16hrs at 75°C. Colorless oil, 98%. ^{31}P NMR ($CDCl_3$): δ +108.7 (d, $^1J_{PH}$=343.3 Hz, $^1J_{PW}$=279.1 Hz). ^1H NMR ($CDCl_3$): δ 7.85 (d, $^2J_{HP}$=343.4 Hz, 1H, PH), 7.49-7.63 (m, 5H, ArH), 3.50 (d, $^3J_{HP}$=12.5 Hz, 3H, OMe).

13: 15 eq. styrene, 17hrs, 75°C, 87%. ^{31}P NMR ($CDCl_3$): δ -153.5 ($^1J_{PW}$=256 Hz, int. 1.0), -148.0 ($^1J_{PW}$=265 Hz, int. 0.4).

14: 15 eq. 2,3-dimethylbutadiene, 17hrs at 75°C, yellow solid, 79%. ^{31}P NMR ($CDCl_3$): δ -137.6 ($^1J_{PW}$=252.1 Hz, int. 1.0). –136.1 ($^1J_{PW}$=258.2 Hz, int. 0.84) **14**; -2.0 (int. 0.08), **15**.

Crystal structure determinations: X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (λ=0.71073 Å) at a temperature of 150(2) K. The structures were refined with SHELXL97[28] against F^2 of all reflections. Illustrations, structure calculations and checking was performed with the PLATON package.[29] Compound **7a**: $C_{21}H_{13}O_5PW$, *Fw* = 560.13, colourless block, 0.30×0.30×0.42 mm^3, orthorhombic, Pnma (No. 62), *a* = 16.6552(3), *b* = 10.3703(1), *c* = 11.7614(2) Å, *V* = 2031.42(5) $Å^3$, *Z* = 4, ρ = 1.831 g cm^{-3}, μ = 5.79 mm^{-1}, 12435 measured reflections, 2422 unique reflections (R_{int} = 0.048). Absorption correction based on multiple measured reflections (correction range 0.27-0.33). Structure solution with Direct Methods.[30] 158 refined parameters, no restraints. *R1/wR2* [$I > 2\sigma(I)$]: 0.0242/0.0594, *R1/wR2* (all reflections) = 0.0277/0.0617. GoF = 1.093. Compound **7b**: $C_{23}H_{18}MnO_2P$, *Fw* = 412.28, orange block, 0.42×0.42×0.60 mm^3, monoclinic, $P2_1/m$ (No. 11), *a* = 8.8819(1), *b* = 10.2680(1), *c* = 10.9361(1) Å, β = 108.6597(4)°, *V* = 944.939(17) $Å^3$, *Z* = 2, ρ = 1.449 g cm^{-3}, μ = 0.80 mm^{-1}, 23479 measured reflections, 2297 unique reflections (R_{int} = 0.078). Absorption correction based on multiple measured reflections (correction range 0.42-0.71). Structure solution with automated Patterson methods.[31] 163 refined parameters, no restraints. *R1/wR2* [$I > 2\sigma(I)$]: 0.0272/0.0747, *R1/wR2* (all reflections) = 0.0296/0.0765. GoF = 1.073. CCDC 253394 (**7a**) and 253395 (**7b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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Supporting Information

Supporting information containing the calculated energies and *xyz*-coordinates of the species discussed is available free of charge via the Internet at http://pubs.acs.org or from the author.

6.5 Notes and References

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Chapter 7

3*H*-Benzophosphepine Complexes: Versatile Phosphinidene Precursors

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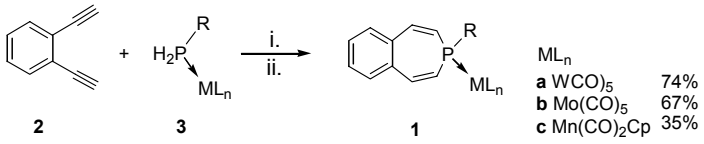
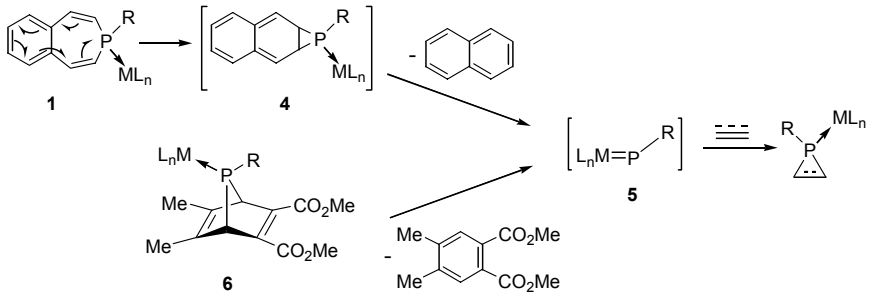
7.1 Introduction

Phosphines are valuable organometallic ligands and are important in catalysts for stereoselective organic reactions. In a continuous demand for atom-efficient, fast, and versatile routes to functionalized phosphines, their reaction with unsaturated bonds (hydrophosphination), especially under catalytic conditions,[1-2] is gaining attention. While radical initiated[3] and base-promoted-[4-5] hydrophosphinations are already known for decades, mechanistic knowledge is required to take better advantage of the more readily occurring reactions when the phosphine is complexed to BH_3[6] or transition-metals,[7-8-9] which both activate the P-H bond.[10] This understanding can aid in the design of selective hydrophosphination catalysts.



Scheme 1- Synthesis of benzophosphepine complexes **1**. i. THF, RT, 12h. ii. KOH, RT.

Because of our recent interest in benzophosphepine complexes **1** (Scheme 1),[11] we were attracted to a report by Märkl and co-workers[12] on the base-catalyzed hydrophosphination of diethynylbenzene **2** with primary phosphines **3**. We found that base (KOH) is required only for full conversion when complexed phosphines are used and that reaction proceeds exclusively in a *trans* fashion at *ambient* temperatures. The present study gives mechanistic details and also insight into the use of the product.



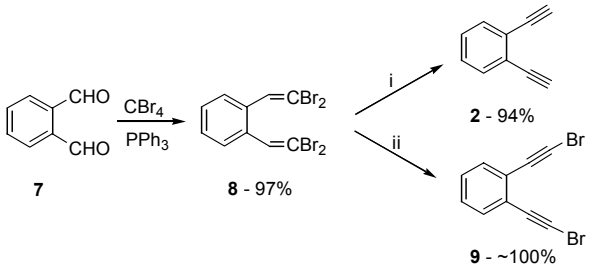
Scheme 2- Isomerization of benzophosphepines **1** and generation of phosphinidenes.

Benzophosphepines have synthetic potential, because they rearrange to the phosphanorcaradienes **4**, *c.f.* the cycloheptatriene-norcaradiene valence isomerization.[13] Phosphanorcaradienes themselves are unstable and dissociate into naphthalene and phosphinidene complexes [R-P=ML_n] (**5**), which are the phosphorus analogues of carbenes (Scheme 2).[14] The electrophilic ones are transient reagents that display a rich and versatile chemistry,[15] but their access has been restricted to only a few synthetic routes[16-17] of which the cheletropic elimination from 7-phosphanorbornadiene complexes **6** is the most used one.[18] Even this reaction is limited to group 6 (Cr, Mo, W) transition metal carbonyl complexes and by the reaction temperature of 110°C. Using CuCl as catalyst lowers the reaction temperature, but it likely also changes the nature of the reagent.[19] Benzophosphepine **1** offers advantages because of its short, convergent synthesis with the phosphorus group being introduced in the last step; access to a broader range of transition metal complexes; a more modest decomposition temperature of 75°-80°C; and a simpler work-up procedure.[11] The applicability of this new complexed phosphinidene precursor will be further detailed with additional mechanistic insights.

7.2 Results and Discussion

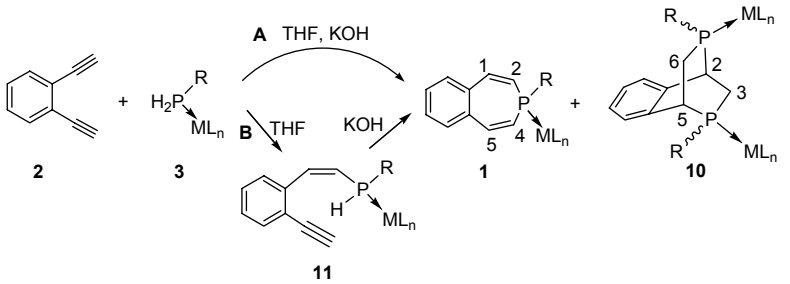
7.2.1 Synthesis of benzophosphepine complexes

Of the two reported syntheses[12,20] leading to 3*H*-benzophosphepines the base-catalyzed hydrophosphination of 1,2-diethynylbenzene is the most attractive one, but requires better access to the dialkyne. An improved synthesis starts with the Corey-Fuchs one carbon homologation[21] of commercially available *o*-phthaldialdehyde (**7**) to give tetrabromide **8**, followed by debromination using LDA to furnish diethynylbenzene **2** in 91% over-all yield (Scheme 3). Bases like *n*-BuLi are less selective. Surprisingly, treatment of **8** with KO*t*Bu at -78°C gave quantitatively the known[22] 1,2-*bis*-(bromoethynyl)benzene **9**, whereas other aromatic bromoalkynes are reported to undergo smooth conversion to terminal alkynes under similar conditions.[23]



Scheme 3 - Synthesis of 1,2-diethynylbenzene. i. 1. LDA, -78°C; 2. $(NH_4)_2SO_4$ aq., -78°C. ii. 1. KO*t*Bu, -78°C; 2. H_2O, -78°C.

We pursued the procedure reported by Märkl *et al.*[12] for the uncomplexed benzophosphepines, but the addition of the various complexed phosphines **3** to diethynylbenzene **2** showed unsatisfactory reproducibility on using KOH with 18-crown-6 in toluene, likely because of its heterogeneous character. This problem was solved by using THF/KOH instead, thereby eliminating the use of the crown ether (Table 1, method A). Unfortunately, similar to the original prodedure, yields never exceeded 50%, despite full consumption of **8** in ca. 10 min. Moreover, this method proved inadequate for the synthesis of 3-amino derivative **1g** because of the instability of the Et_2NPH_2-$W(CO)_5$ complex (**3g**) in THF. This limitation could be overcome by eliminating the use of base entirely for the first hydrophosphination reaction. Thus, monitoring by ^{31}P NMR spectroscopy of the careful addition of an ethereal solution of **3g** to a THF solution of diethynylbenzene showed the appearance of a major resonance at +21 ppm (d, $^1J_{PH}$= 381 Hz), which we assign to the intermediate *cis*-vinylphosphine complex **11g** (Scheme 4, Table 1), and a smaller one at +56 ppm. On addition of KOH full conversion resulted of the signal at +21 ppm into the one at +56 ppm. Work-up of the reaction mixture gave the desired 3-amino-benzophosphepine $W(CO)_5$ complex **3g** in 40% yield as yellow crystals. The same one-pot sequential process, using base to complete the conversion of **11** to **1**, worked also well for the syntheses of several of the other 3*H*-benzophosphepine complexes listed in Table 1 (method B) and for some (**1a**,**b**) with better yields.



Scheme 4 - Synthesis of benzophosphepines **1** with (A) and without (B) initial base, and side-product.

Table 1 - Yields and ^{31}P NMR chemical shifts of 3*H*-benzophosphepine complexes **1** (scheme 4).

	R	ML_n	A[a] (%)	B[b] (%)	^{31}P **1**[c]	^{31}P **11**[d]	$^{1}J_{PH}$[d] (Hz)	^{31}P **3**[d]	Byproduct[e]
a	Ph	$W(CO)_5$	47	74	-14.8	-43	365	-89	-
b	Ph	$Mo(CO)_5$	40	67	5.8	-23	345	-69	A: **10**
c	Ph	$MnCp(CO)_2$	35	-	64.0	-	-	+2[f]	-
d	Ph	$Cr(CO)_5$	37	39	23.1	+2	352	-38	A: polymer?
e	Me	$W(CO)_5$	47	19	-34.2	-69	348	-122	A: **10**
f	*t*-Bu	$W(CO)_5$	41	-	10.5	-	-	-48	-
g	NEt_2	$W(CO)_5$	-	40	+56.8	+21	381	-14	-

[a] Method A, using KOH from the start. [b] Method B, using KOH only for completing the conversion of **11** to **1**. [c] ^{31}P NMR chemical shift ($CDCl_3$) for **1**. [d] ^{31}P NMR chemical shift (THF) for **11** and **3** and coupling constants for **11**. [e] Only when identified. [f] We assign the +2 ppm signal to $(PhPH_2)MnCp(CO)_2$ instead of the reported $(PhPH_2)_2MnCp(CO)$ (ref [24]).

Tolerance of the presented method to variation of both transition metal complexes ($M(CO)_5$ (M = Cr, Mo, W) and $MnCp(CO)_2$) and substituents (Ph, Me, *t*-Bu, and NEt_2) at the phosphorus center is evident (Table 1). Noteworthy is chromium complex **1d**, even though its yield is modest (yellow crystals), because the corresponding phosphanorbornadiene **6d** is difficult to synthesize, which also applies to a lesser extend to the $Mo(CO)_5$-complexes. For this simple reason most phosphinidene chemistry has revolved around the $W(CO)_5$-complexes. The ^{1}H NMR characteristics for **1d** with H(2) and H(4) resonances at 6.18 ppm, a sizable $^{2}J_{HP}$ coupling constant of 24.1 Hz, and a $^{3}J_{HH}$ of 12.4 Hz for the *cis* olefin are also representative for the other benzophosphepine complexes. Using method A enables the synthesis of the sterically demanding *t*-butyl derivative (**1f**, orange crystals), whereas amino derivative **1g** is accessible via method B, as discussed. The large difference in ^{31}P NMR chemical shifts between the methyl and *t*-butyl derivatives (**1e**: -34.5 ppm; **1f**: +10.5 ppm) is due to the substituent effect which is even more pronounced in the phosphine complexes **3**. The low-field ^{31}P NMR chemical shift of **1g** (+56.8 ppm) indicates significant shielding due to electron donation of the nitrogen.

7.2.2 Side-product formation and mechanism

The synthesis of 3-methyl-3*H*-benzophosphepine complex **1f** gives **10e** as byproduct in about 10%, which we believe to be the first complexed 2,5-diphosphabicyclo[2.2.2]octane[25] (or benzeno-1,4-diphosphinane). The *meso* and one of the *rac* isomers that were formed could be isolated by chromatography. The ^{31}P NMR resonances at –15.0 and –16.6 ppm (J_{PP} 17.4 Hz) for the *meso* isomer consist of double doublets indicating non-equivalent phosphorus atoms. The *rac* isomer shows a single ^{31}P NMR resonance at –15.7 ppm, but the complexity of its W-satellites is consistent with the presence of two phosphorus atoms. Also the ^{1}H NMR spectrum of the symmetric **10e** (*rac*) isomer is less complex compared to the asymmetric *meso* isomer. The bridgehead protons give a single resonance at δ 3.64 ppm with a large $^{2}J_{HP}$ of 22.7 Hz and smaller $^{3}J_{HH}$ coupling constants of 5.3 Hz and 2.1 Hz. Two resonances are observed at 2.67 and 2.54 ppm for the *endo*- and *exo*-protons at C3 and C6. All other NMR data of these stable compounds that have melting points > 170°C are consistent with the bicyclo[2.2.2]octane structure **10e**.

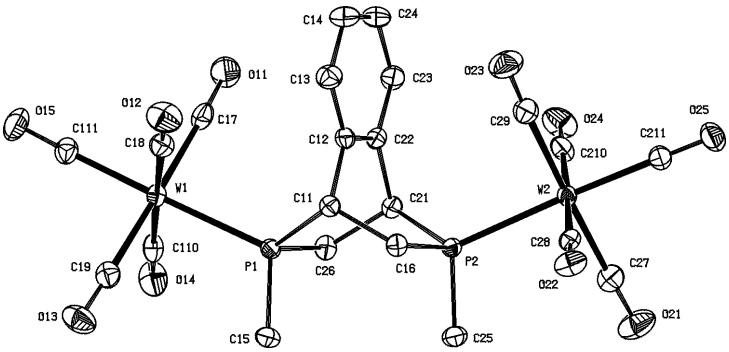


Figure 1 - Displacement ellipsoid plot (50% probability level) of *rac*-**10e**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (deg) and torsion angles (deg): P1-W1 2.5058(7), P2-W2 2.5048(7), P1-C11 1.860(3), P2-C21 1.854(3) P1-C26 1.861(3), P2-C16 1.865(3), P1-C15 1.826(3), P2-C25 1.822(3), C11-C12 1.513(3), C12-C22 1.395(4), C12-C13 1.393(4), P1-C11-C12 105.66(17), P2-C21-C22 105.32(17), P1-C11-C16 113.85(17), P2-C21-C26 113.71(17), C11-C12-C13 123.2(2), C19-W1-P1-C15 12.35(13), C27-W2-P2-C25 11.57(13), C16-C11-C12-C13 –118.3(3), C15-P1-C11-C16 45.8(2), P1-C11-C12-C13 118.5(3).

In the X-ray crystal structure of *rac*-**10e** the molecule has an approximate, non-crystallographic C_2 symmetry. Deviations from the exact symmetry are due to a different arrangement of the $W(CO)_5$-groups, which are both located over the ring-system (Figure 1). The P-CH_3 bond distances are relatively short (1.826(3) and 1.822(3) Å) compared to the P-C bonds in the 1,4-diphosphinane part (1.854(3)-1.865(3) Å). The arrangement around the bridge-head carbon C11 is nearly tetrahedral (Σ 329.4°) and the C-C bonds of the benzene-ring (all 1.386(4)-1.395(4) Å) are indicative of electron delocalization.

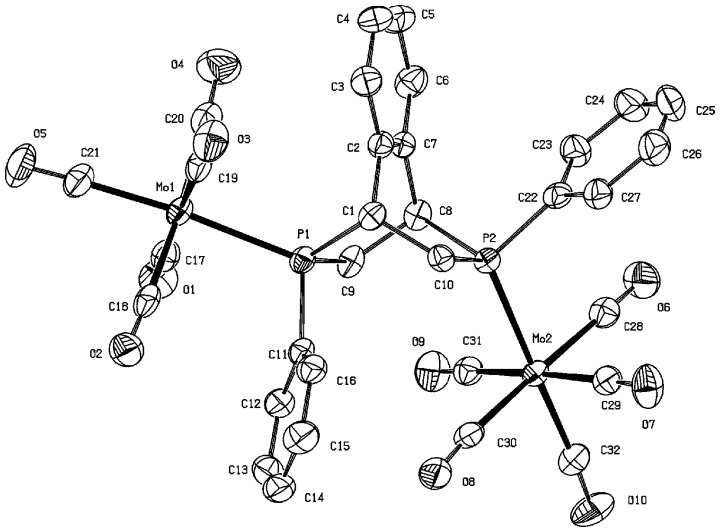
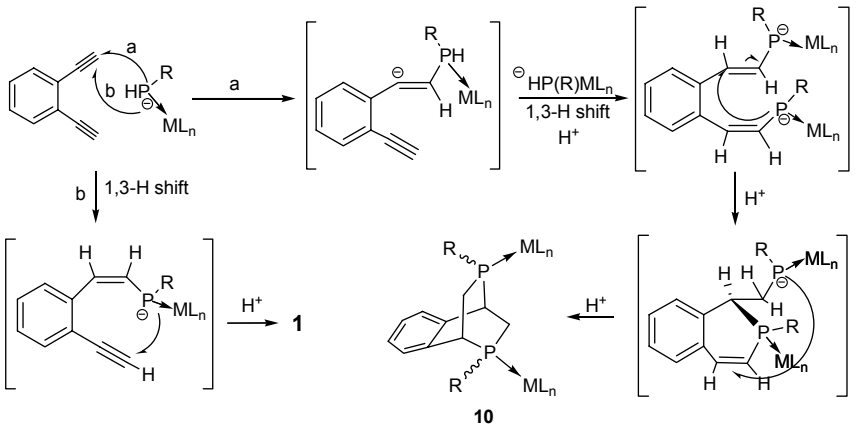


Figure 2 - Displacement ellipsoid plot (50% probability level) of *meso*-**10b**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (deg) and torsion angles (deg): P1-Mo1 2.5099(9), P2-Mo2 2.5237(9), P1-C11 1.826(3), P2-C22 1.830(4), P1-C1 1.850(4), P2-C8 1.861(3), P1-C9 1.855(4), P2-C10 1.863(4), C1-C10 1.533(5), C1-C2 1.515(5), C2-C7 1.396(5), C2-C3 1.393(5), P1-C1-C2 104.4(2), C2-C1-C10 112.6(3), Mo1-P1-C1 119.35(11), Mo2-P2-C8 116.53(11), P1-C1-C2-C3 116.2(3).

$Mo(CO)_5$-complexed diphosphinanes (*rac*- and *meso*-**10b**) were likewise obtained as byproducts (12%) in the synthesis of **1b** (also Method A) and isolated by fractional crystallization. The *rac* isomer has a ^{31}P NMR resonance at δ 19.7 ppm and the asymmetric *meso* isomer two at 27.2 and 25.1 ppm with a $^{3}J_{PP}$ coupling of 11.7 Hz. The molecular structure in the crystal of *meso*-**10b** (m.p. > 116°C), shown in Figure 2, is similar to that of *rac*-**10e**, but the pseudo-symmetric bonds and angles differ slightly due to the asymmetry of the molecule with slightly longer bonds around the P2- than the P1-atom.

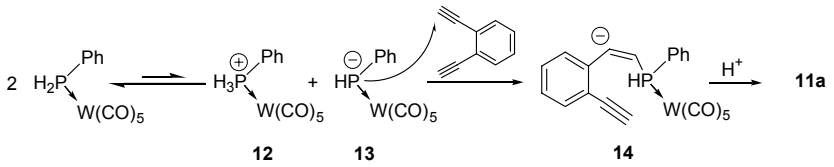
Application of the benzeno-1,4-diphosphinane frame, be it decomplexed, can be envisioned both as a novel ligand system and as a supramolecular building block. Its formation can be explained by successive attacks of two phosphide complexes on diethynylbenzene **2**. The yields increased with an excess of the phosphine complex. The first phosphide attacks a terminal acetylenic carbon in either an *anti* (a) and *syn* (b) fashion (Scheme 5). Route b gives a *cis*-vinylphosphide complex that undergoes intramolecular hydrophosphination to form benzophosphepine **1**. *Anti* attack leads to a *trans* olefin that cannot undergo ring-closure and is therefore subject to attack by a second phosphide complex, either before or after protonation. When this occurs in a *syn* fashion ring-closure at the benzylic carbon will give the Markovnikov addition product and subsequent protonation allows the other phosphorus atom to perform a similar addition to yield 1,4-diphosphinane **10**. When the second phosphide enters in an *anti*-fashion, which may even be sterically preferred, the resulting *bis*-(*trans*-vinylphosphide) is unable to close the ring and may lead to polymeric structures and loss of material.



Scheme 5 - Proposed mechanism for the formation of diphoshabicyclo[2.2.]octanes **10**.

The uncatalyzed reaction of phosphine complexes **3** with 1,2-diethynylbenzene **2** (method B) is truly remarkable because so far all reported hydrophosphinations that used complexed phosphines required heat, base and/or radical initiators,[7,26] except for a report on a room-temperature reaction of ethylene with a Pd-phosphine complex[9] and the facile reaction of a bridged phosphine diiron complex with phenylacetylene.[27]

The first part of the explanation became apparent on mixing equimolar amounts of $PhPH_2$-$W(CO)_5$ and $PhPD_2$-$W(CO)_5$ in anhydrous THF. ^{31}P NMR monitoring showed slow H-D exchange, forming PhPHD-$W(CO)_5$ with a characteristic triplet at –90 ppm, that signifies phosphine disproportionation. The second indicator is the deshielded ^1H NMR chemical shift of the 1,2-diethynylbenzene **2** (3.33 ppm, ≡CH) that suggests an activated acetylenic group similar to benzoylacetylene (3.44 ppm),[28] which readily undergoes phosphine catalyzed additions.[29] Under the same experimental conditions phenylphosphine **3a** reacted hardly with phenylacetylene (3.03 ppm), giving <1% of vinylphosphine, while *p*-diethynylbenzene (3.27 ppm) was only slightly less reactive than **2**. The third, important lead was the NMR identification of vinylphosphine **11d** in the reaction of $PhPH_2$-$Cr(CO)_5$ with **2** (Scheme 4) even though it could not be obtained free of benzophosphepine complex **1d**. The olefinic protons showed a NOE interaction and a coupling constant (12.5 Hz) that are consistent with a *cis* olefin. The ^{31}P NMR chemical shift at +4.3 ppm is similar to the radical initiated hydrophosphination product (+3.4, $^1J_{PH}$ 356 Hz) of $PhPH_2$-$Cr(CO)_5$ (**3d**) with phenylacetylene, which reportedly has a *cis* configuration ($^3J_{HH}$ 13 Hz).[8] Further, ^{31}P NMR monitoring of the reaction of **3d** with **2** in the presence of the radical initiator AIBN showed conversion of the phosphine (**3d**) to vinylphosphine **11d**. Some benzophosphepine **1d** ($\delta(^{31}P)$ 23.1) was also formed, but was not stable at the temperatures required for radical formation (50-60ºC). Finally, ^{31}P-NMR monitoring of the deuterophosphination of **2** with $PhPD_2$-$W(CO)_5$ (**3h**) (with incomplete conversion) showed the formation of only two D-containing products, 1,5-dideuteriophosphepine **1h** (–14.8 ppm, 95% D-label, 14% isolated yield) and a product with a chemical shift at –43.9 ppm (t, $^1J_{PD}$ 55 Hz) that we assign to **11h**.



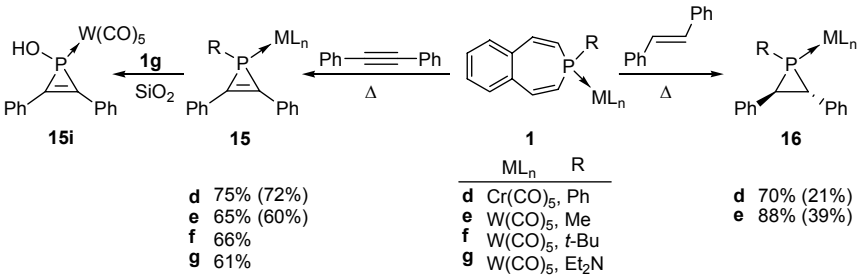
Scheme 6 - Proposed mechanism for the uncatalyzed formation of vinylphosphine complexes.

Consequently, we surmise that the hydrophosphination in THF starts by a little disproportionation of phosphine complex **3** into **12** and **13** of which the phosphide anion attacks the activated acetylenic carbon of **2** to form vinyl-anion **14** that is then protonated (by **12**) to give *cis*-vinylphosphine **11** (Scheme 6). The fact that the phenylphosphine complexes give better yields than the alkylphosphines (Table 1) supports the disproportionation mechanism as the phenyl group stabilizes the charged phosphorus center better.

7.2.3 Reactivity and Kinetics of Benzophosphepines

All the benzophosphepine complexes **1** are phosphinidene precursors as shown by their reaction at 80-85°C (120°C for **1f**) with diphenylacetylene and *trans*-stilbene that afforded the expected phosphirenes **15** and phosphiranes **16**, respectively, in (very) good yields (Scheme 7). The values in parentheses refer to the reported yields for the reaction with phosphanorbornadiene complex **6**.[18,30]

Particularly complexed amino-benzophosphepines are interesting precursors to amino-phosphinidene complexes, which could be trapped upon thermolysis of amino phosphirane complexes in high yields.[17c] The amine group in these trapping products is easily replaced because the amine group is easily replaced, as has been shown, for example, for the corresponding amino phosphirene that converts to the chloro derivative on treatment with dry HCl.[31] We found an unexpected functionalization of the known[32] amino-phosphirene **15g** during its purification over silica, on which it partially converted to the yet unknown hydroxy-phosphirene complex **15i**. This yellow solid (m.p. 122-124°C) has a rather shielded ^{31}P NMR chemical shift at -78.1 ppm with a large $^{1}J_{PW}$ of 319.6 Hz.



Scheme 7 - Phosphinidene addition reactions for **1** with yields in parentheses for those using **6**.

The reaction of the benzophosphepine complexes **1** with phenylacetylene in toluene is a 1st order process for the release of the phosphinidene moiety from **1** that depends more on the substituent than

on the transition metal group. The half-life times, summarized in Table 2, are at 75°C similar for the phenyl derivatives **1a,b,d**; the $t_{1/2}$ of Mn complex **1c** could not be determined accurately due to the broadness of the NMR signals, but the onset of the reaction starts similarly to **1a** at about 50°C. Methyl-substitution (**1e**) increases the half-life time by more than 3 times and that for the *t*-butyl derivative **1f** is about twice as much at the higher temperature of 115°C. The kinetics were determined by ^{31}P NMR for methyl derivative **1e** at four different temperatures (Table 2 right) from which an activation energy is derived of 27.0 ± 0.3 kcal/mol, which is 6 kcal/mol less than for the related decomposition of 7-phenyl-7-phosphanorbornadiene complex **6**.[33] The activation enthalpy is calculated to be 26.3 ± 0.3 kcal/mol, with a small entropy of activation of -5.1 ± 0.9 eu. The rate constants were independent of either the concentration (5.1, 2.6, or 1.0 equivalent) or the nature of the substrate (phenylacetylene, *trans*-stilbene or aniline) in the reaction mixture as graphically shown in Figure 3. This behavior is similar to that reported for **6**.[30,34]

Table 2 - Half-life times of benzophosphepines **1** in the presence of diphenylacetylene (*left*) and the rate-constants for the decomposition of **1e** in the presence of diphenylacetylene (*right*).

Phosphepine 1	T (°C)	$t_{1/2}$ (min)	1e	T (°C)	k (10^{-5} l mol^{-1} s^{-1})
a	75	203		70	1.00
b	75	111		80	3.18
d	75	142		90	9.45
e	75[a]	633		100	24.9
f	115	344		E_a (kcal/mol)	26.3 ± 0.3

[a] Derived from an Arrhenius plot.

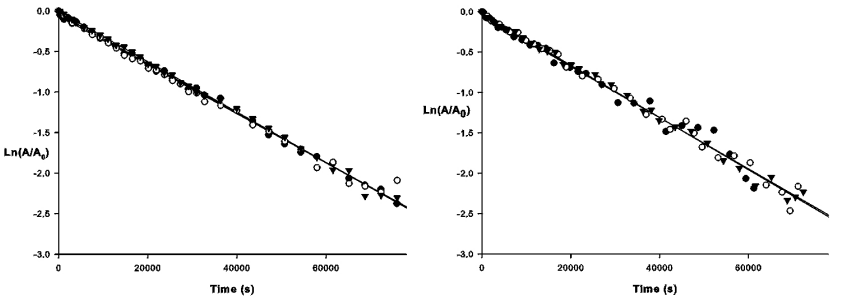


Figure 3 - Kinetic plots of the decomposition of **1e** at 80°C in the presence of: (*left*) aniline (•), 5.1 (o) and 2.6 (▼) eq. stilbene; (*right*) 5.1 (•), 2.6 (▼), 1.0 (o) eq. diphenylacetylene.

To better understand the relationship between the benzophosphepine and 7-phosphanorbornadiene complexes we used density functional theory (B86-P88) for several parent phosphinidene complexes. Their energetic data are summarized in Table 3. The relationship is graphically depicted in Figure 4 for the parent phosphepine-$Cr(CO)_5$ (labeled **I**). Its two conformations with the transition metal group in either an axial (**ax**) or equatorial position (**eq**) interconvert via a ring-flip with a small energy barrier of only 5.9 kcal/mol. Each rearranges in a symmetry-allowed disrotatory process to the corresponding *syn*- or *anti*-phosphanorcaradiene complex (labeled **II**), but these processes are

endothermic by about 3 kcal/mol with barriers of nearly 14 kcal/mol. The higher barrier for ax-**I** → *syn*-**II** may stem from steric interactions between the metal group and the cyclohexadiene ring.

The influence of the transition group on the energy profile is important, but does not discriminate between the metals (entries 2 and 3 of Table 3). Complexation destabilizes norcaradiene **II** with respect to phosphepine **I** and to a smaller extent the transition state for the electrocyclization. Thus, whereas the rearrangement is exothermic for the uncomplexed phosphepine (entry 1), which is indeed an elusive species,[12,20,35] metal-complexation results in an endothermic rearrangement. The influence of the transition metal is evident. Coordination of the phosphorus atom to the transition metal results in strong σ-bonding with electron transfer from the ligand to the metal together with weaker π-back-bonding due to electron donation of the metal into the unoccupied orbitals of the ligand.[36] The P-metal σ-bond diminishes the strength of the phosphirane C-C bonding orbital (Figure 5a), while π-back-donation enhances the anti-bonding nature of the distal C-C bond (Figure 5b). Both effects stabilize the phosphepine over the norcaradiene structure.[37]

Table 3 - B86-P88/*TZP* energies (in kcal/mol) relative to eq-**I**.

Entry	ML_n	R	annelated	syn-II	synTS	ax-I	TS-flip	eq-I	antiTS	anti-II
1	-	H	-	-4.2	10.6	0.0	6.3	0.0	9.7	-4.7
2	$Cr(CO)_5$	H	-	4.4	15.5	1.3	5.9	0.0	13.6	3.1
3	$W(CO)_5$	H	-	3.0	15.1	1.5	6.2	0.0	13.7	2.3
4	$Cr(CO)_5$	Ph[a]	-	2.8	13.5	2.0	5.5	0.0	[c]	2.0
5	$Cr(CO)_5$	Ph[b]	-	3.3	15.3	0.9	4.1	3.7	21.4	7.2
6	-	H	yes	9.6	19.3	-1.3	2.7	0.0	18.0	8.5
7	$Cr(CO)_5$	H	yes	19.1	26.1	0.4	2.8	0.0	24.1	17.6

[a] perpendicular to the P-W bond. [b] parallel to the P-W bond, values relative to eq-I, entry 4. [c] No convergence.

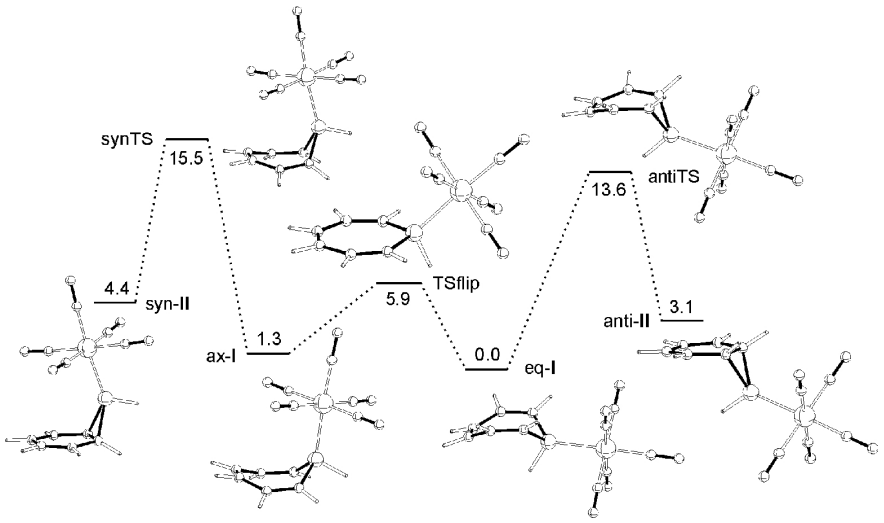


Figure 4 - Energy diagram for the relationship of phosphine-$Cr(CO)_5$ (**I**) and phosphanorcaradiene-$Cr(CO)_5$ (**II**).

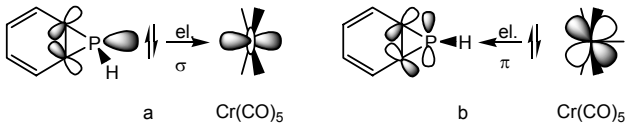
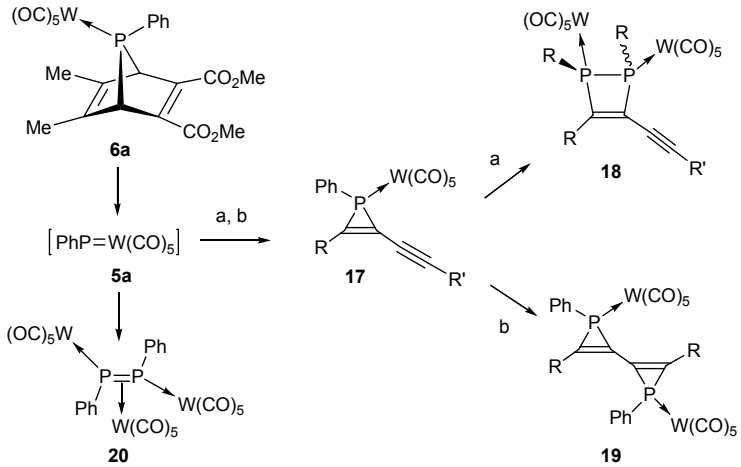


Figure 5 - Schematic representation of the interaction of the Walsh orbitals of phosphanorcaradiene **II** with the orbitals of chromium-pentacarbonyl group.

Substituting hydrogen for a phenyl-group decreases the barrier for electrocyclization slightly (≤ 1.0 kcal/mol, entries 4-5). The phenyl-group can adopt two conformations, either perpendicular or parallel to the P-W bond, the latter of which is found in the crystal structure of $W(CO)_5$-benzophosphepine **1a**, but the difference is marginal for *ax*-**I** and *syn*-**II**; no parallel orientation could be found for the equatorial/anti pair, because it would unfavorably position the phenyl group over the ring.

The effect of benzannellation is far more pronounced, raising the cyclization barrier by about 10 kcal/mol to 26.1 kcal/mol for forming *syn*-benzo-**II** from *ax*-benzo-**I** (entry 6, Table 3), because benzophosphanorcaradiene benefits far less from electron delocalization than benzophosphepine. Dissociation of *syn*-benzo-**II** into $Cr(CO)_5$-phosphinidene and naphthalene is endothermic by 14.9 kcal/mol, but is likely more favorable when the entropy term is included.[38] Recent DFT calculations on $W(CO)_5$-complexed phosphinidenes suggest a small barrier for this process (6.7 kcal/mol).[19]

In summary, ring-closure of metal-complexed benzophosphepine **I** appears to be the rate-determining step, which is in compliance with the kinetic data and with the experimental activation energy of 27.0 kcal/mol for reaction of the $W(CO)_5$-complex **1e**. This is also consistent with the observation that the decomposition of **1e** is neither catalyzed by metals ($PdCl_2$, Pd/C, $CuSO_4$) nor by (Lewis) bases (KOH, Et_3N, BPh_3).



Scheme 8 - Reaction of phosphinidene **5a** with diphenyldiacetylene at (a) 55°C with Cu(I)Cl and (b) 110°C.

Addition to Diynes. Next to turn to is the window within (some of) the benzophosphepines complexes **1** are usable. After all, the electrophilic phosphinidene complexes may add to the C=C bonds **1** possesses and to the C≡CH bonds of their starting material (**2**). We address these aspects starting with a 1,3-diyne. It has been shown that the 'classical' 7-phosphanorbornadiene complex **6a** gives different products depending on the manner in which it is used (Scheme 8). At ca. 55°C, using Cu(I)Cl as catalyst,[18] [1+2] adduct **17** is the primary product. In selected cases, depending on the substituents R and R', a second [PhPW(CO)$_5$] inserts into a C-P bond to give 1,2-diphosphetes **18**.[39] Instead, without using a catalyst (110°C) a second alkyne addition takes place and gives *bis*-phosphirenes **19**.[40] Diphosphene complex **20** is typically observed as a byproduct resulting from the decomposition of **6a**.[33]

Benzophosphepines **1a** (2.2 equiv.) reacted at 60°C with diphenyl-1,3-butadiyne to give the *rac-bis*-phosphirene **19a** (δ ^{31}P -137.3 ppm) as orange needles in 11% yield, a trace of the *meso*-isomer (δ ^{31}P -137.1 ppm), and 28% of mono-adduct **17**[39a] (28%). The low yield of the diadduct is likely due to steric hindrance, which is evident from the single X-ray crystal structure analysis of the *rac*-isomer (Figure 6). In the crystal, the molecule of **19** has only C_1 symmetry. Conjugation of the two phosphirene double bonds is apparent from the short connecting C12-C22 bond (1.423(6) Å), similar to that reported for the di-SiMe$_3$-derivative.[40] In **19** conjugation is extended to the phenyl-substituents, which lie almost in the same plane as the two phosphirene rings (torsion angles of –3.2(9)° and –178.6(6)°).

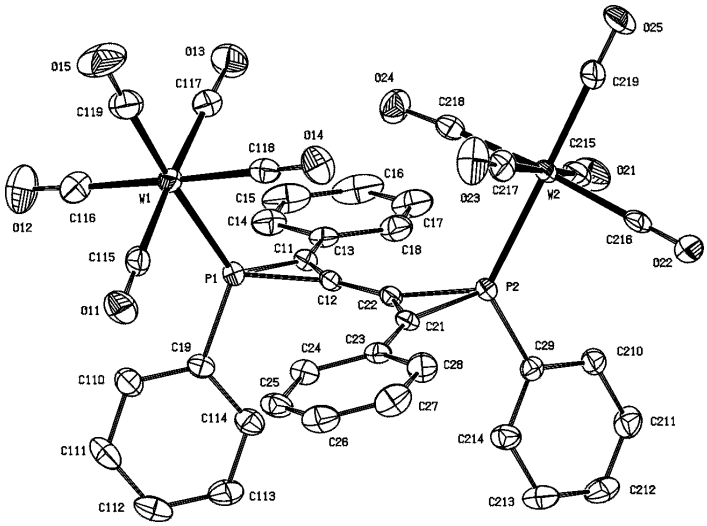
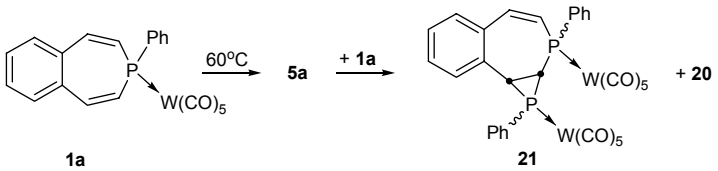


Figure 6 - Displacement ellipsoid plot (50% probability level) of *rac*-**19**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (deg) and torsion angles (deg): W1-P1 2.4905(11), W2-P2 2.4765(10), P1-C11 1.803(4), P1-C12 1.799(4), C11-C12 1.325(6), C21-C22 1.326(6), C12-C22 1.423(6), C11-P1-C12 43.18(18), C21-P2-C22 43.27(18), C11-C12-C22-C-21 –176.1(6), C12-C11-C13-C18 –3.2(9), C22-C21-C23-C28 –178.6(6).

The question arises what the fate is of the reactive phosphinidene in the absence of a substrate. For precursor **6a** this results mostly in diphosphene **20**, which often is also a byproduct of the addition reactions. Monitoring by ^{31}P NMR the decomposition of benzophosphepine **1a** in toluene at 60°C for 3 days likewise resulted in the formation of **20** (10% by ^{31}P NMR), confirming the intermediacy of the same reagent, but in addition gave other products (70% by ^{31}P NMR) that were also observed in the reaction with diphenyldiacetylene. Analysis of the reaction mixture (see Experimental) showed the presence of the four isomers of phosphirane complex **21**, (characteristics are summarized in Table 4), that must result from addition of [PhPW(CO)$_5$] to one of the double bonds of phosphepine **1a** (Scheme 9). The addition underscores the olefinic nature of the phosphepine ring of **1a** as additions to aromatic rings are rare.[41]



Scheme 9 - Reaction of phosphinidene **5a** in the presence of **1a** at 60°C.

Table 4 - ^{31}P NMR chemical shifts (ppm), assignments, and intensities of the isomers of **21**.

21	δ	δ	$^3J_{PP}$ (Hz)	W(CO)$_5$P2	W(CO)$_5$P1	Rel. Int.
a	-8.4	-126.9	14.7	*endo*	*endo*	0.46
b	-6.6	-118.8	11.7	*endo*	*exo*	1.00
c	-15.5	-123.4	11.4	*exo*	*exo*	0.59
d	-16.4	-127.9	14.6	*exo*	*endo*	<0.1

Characteristic in the ^{31}P NMR spectrum of the major isomer **21b** are the double doublets at –6.6 and –118.8 ppm with a $^3J_{PP}$ coupling constant of 11.7 Hz, which enables the assignment of the other isomers as they have different ^{31}P NMR chemical shifts (Table 4). The fact that both the *endo* and *exo* orientations of the W(CO)$_5$P2-moiety are observed is in accord with the calculated modest energy barrier between the axial and equatorial conformations of benzophosphepine complexes. The assignment of **21b** was confirmed by a single crystal X-ray structure determination, which is shown in Figure 7. The W(CO)$_5$ moiety of the phosphepine ring is positioned axially, just as in **1a**, and that of the phosphirane is *exo*-substituted. The P-phenyl substituent is parallel to the almost planar seven-membered ring, thereby rotated by about 90° from its perpendicular position in **1a**. The P-C bond lengths (1.840(2) and 1.839(2) Å) and the C1-P-C2 bond angle (48.74(9)°) for the phosphirane ring are in the expected range.[42]

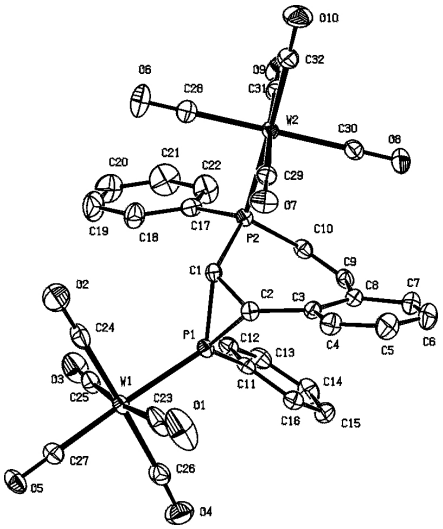
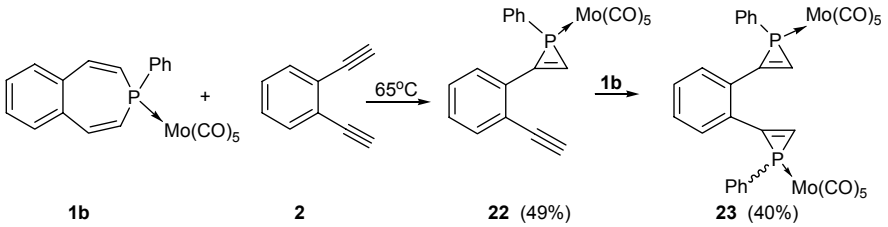


Figure 7 - Displacement ellipsoid plot (50% probability level) of **21b**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (deg) and torsion angles (deg): W1-P1 2.4681(5), W2-P2 2.4960(5), P1-C1 1.840(2), P2-C1 1.814(2), P1-C2 1.860(2), P2-C10 1.799(2), C3-C8 1.412(3), C1-P1-C2 48.74(9), C1-P2-C10 106.17(10), P1-C1-P2 128.77(12), P1-C2-C3 130.22(16), C11-P1-C1-P2 11.47(18), P2-C1-C2-P1 –122.23(16), C8-C9-C10-P2 4.4(4), P2-C1-C2-C3 0.4(3), C28-W2-P2-C17 46.02(11), C23-W1-P1-C11 122.53(12).



Scheme 10 - Reaction of benzophosphepine **1b** with 1,2-diethynylbenzene.

To further establish the reaction window within which the benzophosphepine complexes can be used, it is of interest to verify to what extend they can react with their precursor, 1,2-diethynylbenzene **2**. For this purpose we applied the molybdenum complex **1b** that gave both the mono-adduct **22** (49%) and the di-adduct **23** (40%) in modest yields (Scheme 10), which in part is due to the limited stability of **2** at elevated temperatures. For **23** steric hindrance plays a role. The X-ray crystal structure of *rac*-**23** shows a slightly deformed $Mo(CO)_5$-moiety (Figure 8). The C=C bonds of the phosphirenes are conjugated with each-other via the connecting benzene-ring, as signified by the small dihedral angles and the short C1-C7 (1.456(3) Å) and C2-C9 (1.457(3) Å) bonds. Still, steric bulk prevents the benzene and phosphirene rings to lie in the same plane, causing the P1-phosphirene ring to be tilted by 20º. The other charateristic data of *rac*-**23** in solution (^{31}P δ -135.5 ppm) resemble those of a similar phosphirene molybdenum complex.[43]

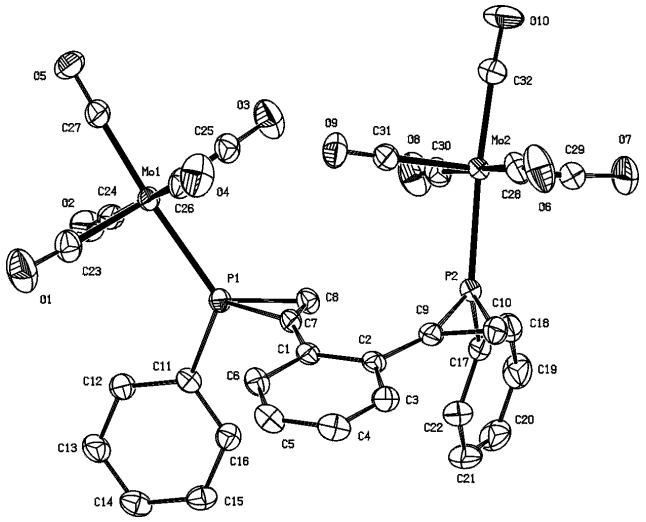
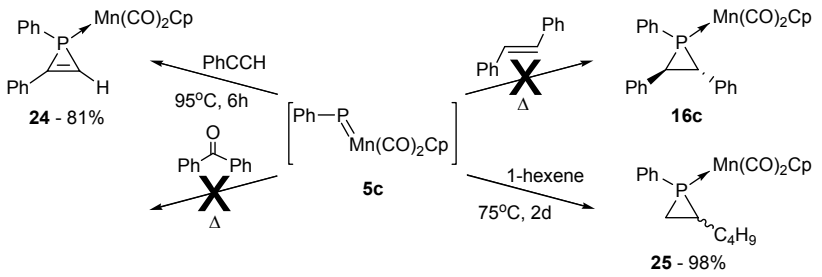


Figure 8 - Displacement ellipsoid plot (50% probability level) of *rac*-**23**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (deg) and torsion angles (deg): Mo1-P1 2.5180(6), Mo2-P2 2.4885(7), P1-C7 1.808(2), P1-C8 1.795(3), P2-C9 1.808(3), P2-C10 1.781(3), C7-C8 1.311(4), C9-C10 1.311(4), C1-C7 1.456(3), C1-C2 1.416(3), C2-C9 1.457(3), C2-C3 1.398(3), C7-P1-C8 42.66(11), C9-P2-C10 42.85(12), C2-C1-C7 123.7(2), C2-C9-C10 139.6(2), P2-C9-C2 152.85(19), C2-C1-C7-P1 177.1(2), C2-C1-C7-C8 21.2(6), C7-C1-C2-C9 5.1(4), C1-C2-C9-C10 177.2(3), C1-C2-C9-P2 –5.0(6), C23-Mo1-P1-C11 42.02(12), C31-Mo2-P2-C17 122.98(12).

Reactivity of a Manganese Phosphinidene. So far we discussed the benzophosphepines **1** as precursors for electrophilic phosphinidenes, such as [RPM(CO)$_5$], but because of its convenient synthesis access to species with other philicities can be envisioned. We will elaborate this aspect for manganese benzophosphepine **1c** on which we reported only briefly in an earlier communication.[11] Presumably [Ph-P=Mn(CO)$_2$Cp] (**5c**) has strongly reduced electrophilic character, since the philicity of a phosphinidene complex [RP=ML$_n$] is known to change profoundly on replacing electron-withdrawing (e.g. CO) for electron-donating ligands such as the cyclopentadienyl ring (Cp).[44] In fact, a number of very stable, highly nucleophilic phosphinidene complexes with rather limited reactivity have been reported. [45] Because both CO and Cp ligands are present in **5c** it is of interest to explore its reactivity.



Scheme 11 - Reactions of phosphinidene **5c** expelled from manganese benzophosphepine **1c**.

Phosphinidene complex **5c** was found to be not nucleophilic enough to react with benzophenone to form a phosphaalkene,[46] nor to be electrophilic enough to yield a P-O ylid either.[47] And although reaction with *trans*-stilbene did not took place, addition to phenylacetylene did occur to give the first manganese complexed phosphirene (**24**) in 81% yield (Scheme 11). The increased electron donation from the transition metal fragment of the yellow product (m.p. 105°C) is apparent from the ^{31}P NMR chemical shift at –59.0 ppm, which is significantly deshielded from that for the phosphirene-M(CO)$_5$ (M = W, Mo) complexes. Phosphirene **24** shows a doublet for its olefinic proton at 8.52 ppm with a large $^2J_{HP}$ of 19.3 Hz. An X-ray crystal structure (Figure 9) supports the formation of the phosphirene, which has a Mn-P bond length (2.1961(6)) similar to that of the benzophosphepine complex **1c**[11] and likewise has its P-phenyl group oriented parallel to this bond. The phosphirene bond lengths and angles are in the expected range.[42] Conjugation between the C1-phenyl group and the phosphirene ring is suggested by the small torsion angle of 5.6(3)°.

The reduced reactivity of [Ph-P=Mn(CO)$_2$Cp] (**5c**) is reminiscent to that of [*i*Pr$_2$N-P=Fe(CO)$_4$], which adds to alkynes and to terminal olefins, but not to di- or higher substituted ones.[16] Reaction of benzophosphepine **1c** in 1-hexene at 70°C gave nearly quantitatively (98%) in a 1:1.4 mixture the *anti*:*syn* phosphirane complexes **25** as a yellow oil (Scheme 11). The ^{31}P NMR chemical shifts of **23** (-77.5/-72.7 ppm) resonate at a distinctly higher field strength than that of phosphirene complex **24** (-59.0 ppm), while the phosphorus in a phosphirene is usually more deshielded than in a less condensed phosphirane. The Mn(CO)$_2$Cp complexed phosphiranes **25** are stable at room temperature, which differs from the Fe(CO)$_4$-complexed ones that are amenable to retro-addition of the phosphinidene.[16] It is evident that **5c** still shows electrophilic behavior although less pronounced than **1a,b**.

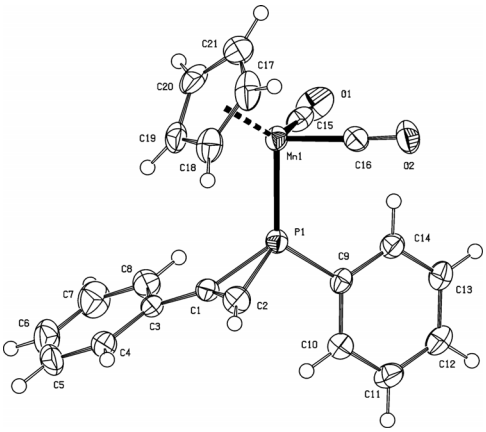


Figure 9 - Displacement ellipsoid plot (50% probability level) of **24**. Selected bond distances (Å), angles (deg) and torsion angles (deg): Mn1-P1 2.1961(5), P1-C1 1.7896(16), P1-C2 1.7781(18), C1-C2 1.310(2), Mn-C15 1.7691(18), Mn-C16 1.7633(18), C15-O1 1.157(2), C1-P1-C2 43.08(8), Mn1-P1-C1 125.48(5), C16-Mn1-P1-C9 –47.71(8), C2-C1-C3-C4 5.6(3).

7.3 Conclusion

We have demonstrated the accessibility of 3*H*-benzophosphepine complexes for a variety of metals and substituents under mild conditions in acceptable yields. As side-products in the synthesis of benzophosphepines novel benzeno-1,4-diphosphinanes were isolated. All of the benzophosphepine complexes eliminate electrophilic phosphinidene complexes at elevated temperatures, as demonstrated by trapping experiments and kinetic analysis, and confirmed by calculations on the proposed mechanism. Compared to others, the lower reaction temperature of this method to generate phosphinidenes enabled the synthesis of a delicate diphosphirene complex. Decomposition of benzophosphepines **1** in the absence of a substrate present results in addition of the phosphinidene complex to a C=C bond of another phosphepine molecule. Currently, we are exploring the use of phosphepines, complexed with other transition metal groups and Lewis acids, to enlarge their scope and applicability.

7.4 Experimental Part

Calculations

All geometry optimizations were performed with the ADF[48] program, using a triple ζ basis set with polarization functions, the local density approximation (LDA) in the Vosko-Wilk-Nusair parameterization[49] with nonlocal corrections for exchange (Becke88)[50] and correlation (Perdew86)[51] included in a selfconsistent manner, and the analytical gradient method of Versluis and Ziegler.[52] Minima were confirmed to have only positive force constant and the transition structures to have only one imaginary value using the *Gaussian98* program package,[53] using geometries optimized with the BP86 exchange-correlation potentials and the LANL2DZ basis set for chromium or tungsten and 6-31G(d) for all other elements.

Synthesis

All experiments were performed under an atmosphere of dry nitrogen. All solvents were distilled from $LiAlH_4$ (pentane, diethylether), sodium benzophenone (THF) or P_2O_5 (dichloromethane) before use. Diisopropylamine was distilled from KOH. $W(CO)_5(MePH_2)$, $W(CO)_5tBuPH_2$, $Cr(CO)_5(PhPH_2)$ were synthesized according to literature procedures.[54] The synthesis of $W(CO)_5(Et_2NPH_2)$ (**3g**) has been described briefly before.[55] All other compounds were purchased and used as such. NMR spectra were recorded on Bruker AC 200 (^1H, ^{13}C), Bruker WM 250 (^1H, ^{13}C, ^{31}P) and Bruker MSL 400 MHz (^1H, ^{13}C) spectrometers, IR spectra on a Mattson-6030 Galaxy FT-IR spectrophotometer and high-resolution mass spectra (HRMS) on a Finnigan MAT 900 spectrometer. NMR-chemical shifts are internally referenced to the solvent for ^1H ($CDCl_3$: 7.25 ppm, C_6D_6: 7.15 ppm) and ^{13}C ($CDCl_3$: 77.0 ppm, C_6D_6: 128 ppm) and externally for ^{31}P to 85% H_3PO_4.

1,2-*bis*-(2',2'-dibromoethenyl)benzene (8): Triphenylphosphine (27.52 g, 104.9 mmol) was added portion-wise to a cold (0°C) solution of tetrabromomethane (17.39 g, 52.4 mmol) in 250 mL dichloromethane. The resulting orange-red solution was stirred at room-temperature for 20 min. After cooling to 0°C a solution of 3.07 g (22.8 mmol) *o*-phtaldialdehyde in 100 mL dichloromethane was added slowly and the mixture was stirred in the dark at room-temperature for 2hrs. The reaction mixture was extracted with distilled water (2x100 mL) and the water-layers washed with dichloromethane (2x50mL). The combined organic layers were dried ($MgSO_4$) and concentrated. Pentane (7x150 mL) was added and the resulting suspension was decanted after stirring. After addition of another 150 mL of pentane to the suspension it was filtered and all pentane fractions were combined, concentrated and purified by column chromatography (SiO_2, 1% Et_2O in pentane, R_f=0.5), yielding a yellow oil (9.85 g, 22.1 mmol, 97%). ^{13}C NMR ($CDCl_3$): δ 135.4 (CH=), 134.58 (*ipso*-ArC), 128.8 (*o*-ArC), 128.4 (*m*-ArC), 93.1 (=CBr_2). ^1H NMR ($CDCl_3$): δ 7.47-7.56 (m, 2H, *o*-ArH), 7.42 (s, 2H, CH=), 7.35-7.39 (m, 2H, *m*-ArH). HRMS: Calcd for $C_{10}H_6{}^{79}Br_2{}^{81}Br_2$: 445.71620. Found: 445.71701. M/*z* (%): 446 (5) [M^+], 367 (20) [M^+-Br], 286 (100) [M^+-^{81}Br-^{79}Br], 126 (38) [M^+-Br_4].

1,2-Diethynylbenzene (2): 48.8 mL (78.1 mmol) *n*-BuLi (1.6 M in hexanes) was added to a cold (-78°C) solution of 10.3 mL (78.1 mmol) diisopropylamine in 250 mL THF. After warming up to room-temperature the solution was added carefully to a cold (-78°C) well-stirred solution of 5.82 g (13.0 mmol) **8** in 50 mL THF. After 20 min. stirring at -78°C the reaction was quenched with 130 mL sat. $(NH_4)_2SO_4$ aq. and stirred for 2hrs at room-temperature. The reaction mixture was poured out in

200 mL pentane, the organic layer was separated and washed with water, dried ($MgSO_4$), concentrated and purified using column chromatography (SiO_2, 1% Et_2O in pentane, R_f=0.42), yielding a colorless liquid (1.54 g, 12.2 mmol, 94%). ^{1}H NMR ($CDCl_3$): δ 7.48-7.54 (m, 2H, *o*-ArH), 7.27-7.34 (m, 2H, *m*-ArH), 3.33 (s, 2H, CH).

1,2-*bis*-(Bromoethynyl)benzene (9): To a cold (-78°C) solution of **8** (0.3 mmol) in THF (3 mL) was added KO*t*Bu (0.5 g, 5.3 mmol). After 5 min. brine (3.8 mL) was added and the solution was allowed to warm up to room temperature. The organic layer was separated and the water layer extacted with diethylether (3x5 mL). The combined organic layers were dried ($Na2SO_4$) and after evaporation of the solvent, the crude product was purified by filtration over a short silica plug, eluting with 1% Et_2O in pentane, yielding a clear oil (0.084 g, 0.3 mmol, ~100%). ^{13}C NMR ($CDCl_3$): δ 132.8 (s, ArC), 128.7 (s, ArC), 126.2 (s, *ipso*), 78.8 (s, Ar-C≡), 54.5 (s, ≡CBr). ^{1}H NMR ($CDCl_3$): δ 7.37-7.41 (m, 2H, ArH), 7.21-7.25 (m, 2H, ArH).

(*N*,*N*-Diethylamino) phosphine pentacarbonyltungsten(0) (3g): To a solution of dichloro (*N*,*N*-diethylamino) phosphine[56] (1.76 g, 10.1 mmol) in THF (80 mL) a mixture of $W(CO)_5$AcCN and $W(CO)_5NMe_3$ (3.75 g , 10.0 mmol) was added. The resulting green solution was protected from light and stirred for 3 days at 45°C. The mixture was concentrated, and filtered over a short silica plug, eluting with diethylether. Evaporation gave a yellow powder (3.57 g, 7.5 mmol, 75%). ^{31}P NMR ($CDCl_3$): δ 124.01 ($^1J_{PW}$=378.5 Hz). ^{1}H NMR ($CDCl_3$): δ 3.44-3.59 (m, 4H, CH_2N), 1.25 (m, 6H, CH_3).

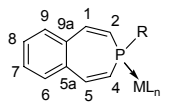
To a cold (0°) stirred suspension of $LiAlH_4$ (0.58 g, 15.3 mmol) in diethylether (20 mL) was carefully added a solution of dichloro (*N*,*N*-diethylamino) phosphine pentacarbonyltungsten(0) (3.64 g, 7.3 mmol) in diethylether (24 mL). After one hour stirring at room-temperature acrylonitril was added (1.0 mL), the suspension was filtrated and the solvent evaporated, yielding a yellow oil (1.76 g, 4.1 mmol, 56%), which was immediately dissolved in diethylether. ^{31}P-NMR (Et_2O): δ -12.1 ($^1J_{PW}$=245.0 Hz)

***P,P*-Dideuteriophenylphosphine pentacarbonyltungsten(0) (3h): 3a** (0.71 g, 1.6 mmol) was dissolved in THF (3 mL), D_2O (1.8 mL) was added and the resulting mixture was stirred well. THF was evaporated, pentane added and the D_2O layer was separated. ^{31}P NMR analysis of the pentane layer showed incomplete conversion so pentane was evaporated and the procedure repeated twice. Upon complete conversion the pentane layer was filtered over little Na_2SO_4 and concentrated. At –20°C light yellow plates were formed (0.52 g, 1.2 mmol, 72%). Mp: 47-48°C. ^{31}P NMR (C_6D_6): δ -89.6 (q, $^1J_{PD}$=52.9 Hz, $^1J_{PW}$=220.5 Hz, int. 100, PD_2), -88.9 (t, $^1J_{PD}$=52.9 Hz, int. 4, PHD). ^{13}C NMR (C_6D_6): δ 198.4 (d, $^2J_{CP}$=21.8 Hz, CO_{ax}), 195.8 (d, $^2J_{CP}$=6.9 Hz, $^1J_{CW}$=125.0 Hz, CO_{eq}), 132.7 (d, $^2J_{CP}$=11.4 Hz, *o*-ArC), 130.5 (d, $^4J_{CP}$=2.3 Hz, *p*-ArC), 129.0 (d, $^3J_{CP}$=10.4 Hz, *m*-ArC), 125.3 (d, $^1J_{CP}$=48.1 Hz, *ipso*-ArC). ^{1}H NMR (C_6D_6): δ 6.94-7.05 (m, 2H, *o*-H), 6.86-6.91 (m, 3H, *m*+*p*-H), 4.73 (dm, $^1J_{HP}$=344.1 Hz, rel. int. 0.02, PHD). IR (KBr): ν = 2076.6 (m), 1996.6 (m), 1949.7 (s), 1913.7 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{11}H_5D_2O_5PW$: 435.96639. Found: 435.96726. M/*z* (%): 436 (48) [M^+], 380 (52) [M^+-2CO], 350 (92) [M^+-3CO-D], 348 (100) [M^+-3CO-D_2], 320 (50) [M^+-4CO-D_2], 292 (70) [M^+-5CO-D_2].

General synthesis of 3*H*-3-benzophosphepine complexes 1:

Method A (with base): The appropriate phosphine complex (1 mmol) and 1,2-diethynylbenzene (1.5 mmol) were dissolved in THF (11.75 mL) followed by addition of freshly grounded KOH (79 mg). Almost immediately a color-change took places and after completion of the reaction the mixture was filtered over a short silica column, the solvent was evaporated and the excess 1,2-diethynylbenzene distilled off at 50°C/1 mm Hg. The crude product was purified by column chromatography (toluene:pentane=1:4) and subsequently crystallized from diethylether:pentane=1:4 at –20°C.

Method B (without initial base): The appropriate phosphine complex (1 mmol) and 1,2-diethynylbenzene (1.3 mmol) were dissolved in THF (11.75 mL). After 2-3hrs freshly grounded KOH (50 mg) was added. Work-up as above.



3-Phenyl-*3H*-3-benzophosphepine pentacarbonylchromium(0) (1d): According to general synthesis, 10 min. stirring. Yellow plates, 37 %. Mp (decomp): 114 °C. ^{31}P NMR ($CDCl_3$): δ 23.1. ^{13}C NMR ($CDCl_3$): δ 221.6 (d, $^2J_{CP}$=7.4 Hz, CO_{ax}), 216.3 (d, $^2J_{CP}$=13.6 Hz, CO_{eq}), 141.0 (d, $^2J_{CP}$=3.4 Hz, C1, C5), 136.6 (d, $^3J_{CP}$=4.4 Hz, C5a, C9a), 135.8 (d, $^1J_{CP}$=41.5 Hz, *ipso*-ArC), 132.4 (d, $^4J_{CP}$=0.8 Hz, C6, C9), 131.1 (d, $^2J_{CP}$=11.0 Hz, *o*-ArC), 129.7 (d, $^4J_{CP}$=2.2 Hz, *p*-ArC), 128.4 (d, $^3J_{CP}$=9.6 Hz, *m*-ArC), 128.1 (s, C7, C8), 126.6 (d, $^1J_{CP}$=32.6 Hz, C2, C4). ^{1}H NMR ($CDCl_3$): δ 7.56-7.64 (m, 2H, *o*-ArH), 7.14-7.37 (m, 5H, *m*+*p*-ArH+H1+H5), 7.29 (s, 4H, H(C6-C9)), 6.18 (dd, $^2J_{HP}$=24.1 Hz, $^3J_{HH}$=12.4 Hz, 2H, H2+H4). IR (KBr): ν = 2063.9 (s), 1924.0 (s), 1898.7 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{21}H_{13}CrPO_5$, 427.9906. Found 427.9886. M/*z* (%): 428 (16) [M^+], 288 (100) [M^+-5CO], 160 (55) [M^+-5CO-$C_{10}H_8$], 128 (16) [$C_{10}H_8^+$].

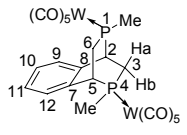
3-Methyl-3*H*-3-benzophosphepine pentacarbonyltungsten(0) (1e): General synthesis, but 2 equiv. of 1,2-diethynylbenzene. 10 min. stirring. Large light yellow needles, 47%. Mp (decomp): 105-106°C. ^{31}P NMR ($CDCl_3$): δ -34.2 ($^1J_{PW}$=231.3 Hz). ^{13}C NMR ($CDCl_3$): δ 199.8 (d, $^2J_{CP}$=19.6 Hz, CO_{ax}), 196.3 (d, $^2J_{CP}$=7.1 Hz, CO_{eq}), 140.1 (s, C1, C5), 136.7 (d, $^3J_{CP}$=5.6 Hz, C5a, C9a), 132.4 (s, C6, C9), 128.0 (s, C7, C8), 129.8 (d, $^1J_{CP}$=35.9 Hz, C2, C4), 18.7 (d, $^1J_{CP}$=33.9 Hz, CH_3P). ^{1}H NMR ($CDCl_3$): δ 7.33 (s, 4H, H6-H9), 7.06 (ddd, $^3J_{HP}$=33.8 Hz, $^3J_{HH}$= 12.7 Hz, $^4J_{HH}$=2.3 Hz, 2H, H1+H5), 5.93 (dd, $^2J_{HP}$=18.7 Hz, $^3J_{HH}$= 12.7 Hz, 2H, H2+H4), 1.91 (d, $^2J_{HP}$=7.4 Hz, 3H, CH_3P). IR (KBr): ν = 2067.8 (s), 1913.5 (s) (C≡O) cm^{-1}. HRMS: Calculated for $C_{16}H_{11}O_5PW$: 497.9853, found: 497.9839. M/*z* (%): 498 (57) [M^+], 414 (100) [M^+-3CO], 356 (85) [M^+-H_2-5CO], 128 (17) [$C_{10}H_8^+$].

3-*t*-Butyl-3*H*-3-benzophosphepine pentacarbonyltungsten(0) (1f): General synthesis, 1h45 stirring. Orange plates, 41 %. Mp: 95°C. ^{31}P NMR ($CDCl_3$): δ 10.5 ($^1J_{PW}$=233.4 Hz). ^{13}C NMR ($CDCl_3$): δ 199.8 (d, $^2J_{CP}$=20.4 Hz, CO_{ax}); 197.0 (d, $^2J_{CP}$=6.8 Hz, CO_{eq}), 140.9 (d, $^2J_{CP}$=3.9 Hz, C1, C5), 136.5 (d, $^3J_{CP}$=3.6 Hz, C5a, C9a), 133.7 (s, C6, C9), 128.6 (s, C7, C8), 123.2 (d, $^1J_{CP}$=31.5 Hz, C2, C4), 33.6 (d, $^1J_{CP}$=26.6 Hz, $\underline{C}Me_3$), 26.6 (d, $^2J_{CP}$=5.1 Hz, CH_3). ^{1}H NMR ($CDCl_3$): δ 7.26-7.34 (m, 4H, H(C6-C9)), 7.03 (ddd, $^3J_{HP}$=31.2 Hz, $^3J_{HH}$=13.6 Hz, $^5J_{HH}$=2.9 Hz, 2H, H1+H5), 5.92 (dd, $^2J_{HP}$=19.4 Hz, $^3J_{HH}$=13.6 Hz, 2H, H2+H4), 1.34 (d, $^3J_{HP}$=14.9 Hz, 9H, CH_3). IR (KBr): ν = 2068.0 (s), 1995.4 (s), 1981.6 (s), 1944.7 (s), 1920.6 (sh), 1904.5 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{19}H_{17}WPO_5$: 540.03235. Found: 540.03104.

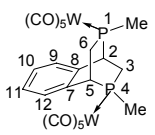
3-Diethylamino-3*H*-3-benzophosphepine pentacarbonyltungsten(0) (1g): A solution of **3g** (0.33 mmol, 1.3 mL, 0.25 M in Et_2O) was added slowly under stirring to a solution of **2** (25 mg, 0.20 mmol) in THF (0.4 mL) at room-temperature. The reaction mixture was stirred overnight, freshly ground KOH (30 mg) was added, and after 2h15 min filtered over a short silica plug. After evaporation the crude product was purified by column chromatography (SiO_2, 1:4=toluene:pentane) and crystallization (Et_2O:pentane=1:4). Yellow blocks, 40%. Mp (decomp.): 97°C. ^{31}P NMR ($CDCl_3$): δ 56.8 ($^1J_{PW}$=261.0 Hz). ^{13}C NMR ($CDCl_3$): δ 200.3 (d, $^2J_{CP}$=21.2 Hz, CO_{ax}), 196.6 (d, $^2J_{CP}$=7.2 Hz, $^1J_{CW}$=126.2 Hz, CO_{eq}), 137.4 (s, C1, C5), 136.3 (d, $^3J_{CP}$=3.8 Hz, C5a, C9a), 133.5 (s, C6, C9), 130.8 (d, $^1J_{CP}$=38.9 Hz, C2, C4), 128.3 (s, C7, C8), 42.7 (d, $^2J_{CP}$=5.8 Hz, CH_2), 14.6 (d, $^3J_{CP}$=2.8 Hz, CH_3). ^{1}H NMR ($CDCl_3$): δ 7.24-7.28 (m, 4H, H(C6-C9)), 6.83 (ddd, $^3J_{HP}$=35.0 Hz, $^3J_{HH}$=13.2 Hz, $^4J_{HH}$=3.1 Hz, 2H, H1+H5), 5.87 (dd, $^2J_{HP}$=15.6 Hz, $^3J_{HH}$=13.2 Hz, 2H, H2+H4), 3.30 (dq, $^3J_{HP}$=11.9 Hz, $^3J_{HH}$=7.0 Hz, 4H, CH_2), 1.15 (t, $^3J_{HH}$=7.0 Hz, 6H, CH_3). IR (KBr): ν = 2071.2 (m), 1986.7 (s), 1938.7 (sh), 1917.7 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{19}H_{18}NO_5P^{182}W$: 553.04051. Found: 553.04061. Calcd for $C_{19}H_{18}NO_5P^{186}W$: 557.04666. Found: 557.04644. M/*z* (%): 555 (48) [M^+], 471 (100) [M^+-3CO], 415 (50) [M^+-5CO], 128 (72) [$C_{10}H_8^+$].

3-Phenyl-1,5-dideuterio-3*H*-benzophosphepine pentacarbonyltungsten(0) (1h): To a solution of **3h** (135 mg, 0.31 mmol) in THF (5.7 mL) was added 1,2-diethynylbenzene (0.8 ml, 0.5 M in THF, 0.4 mmol). The mixture was stirred for 1 day at room temperature and 7h at 35°C, followed by filtration over a silica plug and purification by column chromatography (1st 1:4=toluene:pentane, 2nd 2:3=toluene:pentane). **1h** was obtained in pure form by crystallization (-20°C) from 1:4=Et_2O:pentane. Light yellow plates, 25 mg, 0.044 mmol, 14%, >94% D_2. Mp (decomp): > 110 °C. ^{31}P NMR ($CDCl_3$): δ -14.8 ($^1J_{PW}$ = 236.8 Hz). ^{13}C NMR ($CDCl_3$): δ 199.6 (d, $^2J_{CP}$ = 20.5 Hz, CO_{ax}), 196.4 (d, $^2J_{CP}$ = 7.0 Hz, $^1J_{CW}$ = 126.0 Hz, CO_{eq}), 140.3 (t, $^1J_{CD}$ = 24 Hz, C1, C5), 136.4 (d, $^3J_{CP}$ = 4.7 Hz, C5a, C9a), 135.5 (d, $^1J_{CP}$ = 46.2 Hz, *ipso*-C), 132.7 (s, C6, C9), 132.2 (d, $^2J_{CP}$ = 12.2 Hz, *o*-ArC), 130.2 (d, $^4J_{CP}$ = 2.1 Hz, *p*-ArC), 128.6 (d, $^3J_{CP}$ = 10.0 Hz, *m*-ArC), 128.1 (s, C7, C8), 127.3 (d, $^1J_{CP}$ = 36.6 Hz, C2, C4). ^{1}H NMR ($CDCl_3$): δ 7.70-7.75 (m, 2H, *o*-ArH), 7.37-7.47 (m, 3H, *m*+*p*-ArH), 7.31 (s, 4H, H6-H9), 6.10 (d, $^2J_{HP}$ = 21.3 Hz, 2H, H2+H4). IR (KBr): ν = 2069.2 (m), 1948.0 (s), 1928 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{21}H_{11}D_2O_5WP$: 562.01334 Found 562.01359. M/*z* (%): 562 (35) [M^+], 478 (100) [M^+-3CO], 420 (100) [M^+-5CO-D/H_2], 130 (100) [$C_{10}H_6D_2^+$].

1,4-Dimethyl-2,5-[1,2]-benzeno-1,4-diphosphinane bis (tungsten(0)pentacarbonyl) (10e): 3e (185 mg, 0.497 mmol) and **2** (50 mg, 0.4 mmol) were dissolved in THF (5.8 mL). Freshly ground KOH (70 mg) was added and the solution turned immediately red. After stirring overnight the red and cloudy solution was filtered over silica, eluted with THF and concentrated. The residu was purified by column chromatography (toluene:pentane:THF=17:66:1) yielding several fractions. The 1st fraction (R_f=0.57) contained benzophosphepine **1e** (50.3 mg, 25%). Fraction 2 (R_f=0.36) mainly (~75%) *meso*-**10e** part of which could obtained pure after succesive crystallizations from hexane/dichloromethane. Fraction 3 (R_f=0.13): *rac*-**10e** (54.1 mg, 14%). Small, yellowish needles could be obtained from chloroform or diethylether.



meso-**10e**



rac-**10e**

***meso*-10e:** Mp: 174-175°C. ^{31}P NMR ($CDCl_3$): δ -15.0 (d, $^3J_{PP}$=17.4 Hz, $^1J_{PW}$=246.9 Hz), -16.6 (d, $^3J_{PP}$=17.4 Hz, $^1J_{PW}$=235.0 Hz). ^{13}C NMR ($CDCl_3$): δ 198.6 (d, $^2J_{CP}$=23.5 Hz, CO_{ax}), 197.6 (d, $^2J_{CP}$=22.2 Hz, CO_{ax}), 196.7 (d, $^2J_{CP}$=6.7 Hz, $^1J_{CW}$=118.1 Hz, CO_{eq}), 196.0 (d, $^2J_{CP}$=7.1 Hz, $^1J_{CW}$=132.6 Hz, CO_{eq}), 135.8 (m, C7), 134.3 (dd, $^2J_{CP}$=6.6 Hz, $^3J_{CP}$=1.8 Hz, C8), 129.0-129.2 (m, C9-C11), 128.0 (t, $^3J_{CP}$=$^4J_{CP}$=3.2 Hz, C12), 39.1 (dd, $^1J_{CP}$=20.4 Hz, $^2J_{CP}$=5.7 Hz, C5), 38.5 (dd, $^1J_{CP}$=19.8 Hz, $^2J_{CP}$=5.8 Hz, C2), 30.0 (dd, $^1J_{CP}$=26.9 Hz, $^2J_{CP}$=6.0 Hz, C6), 29.1 (dd, $^1J_{CP}$=21.6 Hz, $^2J_{CP}$=5.5 Hz, C3), 22.1 (d, $^1J_{CP}$=28.7 Hz, CH_3P4), 19.9 (d, $^1J_{CP}$=18.4 Hz, CH_3P1). ^{1}H NMR ($CDCl_3$): δ 7.37-7.43 (m, 3H, H9-H11), 7.19-7.21 (m, 1H, H12), 3.67 (dddd, $^2J_{HP}$=19.9 Hz, $^3J_{HP}$=5.0 Hz, $^3J_{HH}$=5.1, $^3J_{HH}$=2.1 Hz, 1H, H2), 3.40 (ddm, $^2J_{HP}$=19.9 Hz, $^3J_{HH}$=4.1 Hz, H5), 2.77 (dddm, $^3J_{HP}$=7.5 Hz, $^2J_{HH}$=15.1 Hz, $^3J_{HH}$=2.1 Hz, 1H, H3a), 2.61 (dm, $^3J_{HH}$=4.1 Hz, 2H, H6a-b), 2.07 (d, $^2J_{HP}$=6.1 Hz, 3H, CH_3P1), 1.98 (ddm, $^2J_{HH}$=15.1 Hz, $^3J_{HH}$=5.1 Hz, 1H, H3b), 1.04 (d, $^2J_{HP}$=5.9 Hz, 3H, CH_3P4). IR (KBr): ν = 2068.0 (s), 1982.0 (s), 1952.3 (sh), 1939.6 (sh), 1921.3 (sh), 1910.6 (sh), 1899.9 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{22}H_{16}W_2P_2O_{10}$, 869.9237. Found 869.92623. M/*z* (%): 870 (100) [M^+], 786 (92) [M^+-3CO], 758 (52) [M^+-4CO].

***rac*-10e:** Mp: 170°C > decomposition. ^{31}P NMR ($CDCl_3$): δ -15.7 ($^1J_{PW}$=249.2 Hz). ^{13}C NMR ($CDCl_3$): δ 198.7 (m, CO_{ax}), 196.0 (m, CO_{eq}), 136.0 (m, C7, C8), 129.6 (m, C10, C11), 129.1 (m, C9, C12), 38.4 (m, C2, C5), 28.6 (m, C3, C6), 19.0 (m, CH_3). ^{1}H NMR ($CDCl_3$): δ 7.40 (s, 4H, H9-H12), 3.64 (ddd, $^2J_{HP}$=22.7 Hz, $^3J_{HH}$=5.3 Hz, $^3J_{HH}$=2.1 Hz, 2H, H2, H5), 2.67 (ddm, $^2J_{HH}$=14.9 Hz, $^3J_{HH}$=2.1 Hz, 2H, H3a, H6a), 2.54 (ddm, $^2J_{HH}$=14.9 Hz, $^3J_{HH}$=5.3 Hz, 2H, H3b, H6b). 2.07 (d, $^2J_{HP}$=6.1 Hz, 6H, CH_3P). IR (KBr): ν = 2068.1 (m), 1985.4 (m), 1926.4 (s), 1909.8 (s), 1895.0 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{22}H_{16}W_2P_2O_{10}$, 869.9238, Found, 869.9254. M/*z* (%): 870 (<1) [M^+], 590 (<1) [M^+-10CO], 472 (20) [M^+-10CO-CH_3-C_8H_7], 430 (100) [$W_2P_2^+$].

1,4-Diphenyl-2,5-[1,2]-benzeno-1,4-diphosphinane bis (molybdenum(0) pentacarbonyl) (10b): To a suspension of KOH (0.24 g) in THF (16.0 mL) was added simultaneously a solution of **2** (0.85 mmol, 0.5 M in THF, 1.7 mL) and **3b** (1.47 mmol, 0.49 M in THF, 3.0 mL). The solution turned red immediately and was stirred overnight at room-temperature. After filtration over a short silica plug and evaporation of the solvent the crude product mixture was separated by column chromatography (Et_2O:pentane=1:4) yielding several fractions. The 1st fraction (R_f=0.57) contained mostly benzophosphepine **1b**, which was purified by crystallization (43.1 mg, 0.091 mmol, 11%). The second fraction (R_f=0.43, 106 mg) was a mixture of the benzophosphepine (5%) and the two isomers of **10b** (*rac*: 67%, *meso*: 29%). *rac*-**10b** could be isolated in pure form after fractional crystallization from DCM/pentane. *meso*-**10b** could be obtained almost pure (>95%), also by crystallization from DCM/pentane.

***meso*-10b:** Colorless blocks. Mp: decomposition >163°C. ^{31}P NMR ($CDCl_3$): δ 27.2 (d, $^3J_{PP}$=11.7 Hz), 25.1 (d, $^3J_{PP}$=11.7 Hz). ^{13}C NMR ($CDCl_3$): δ 209.8 (d, $^2J_{CP}$=25.2 Hz, CO_{ax}), 208.9 (d, $^2J_{CP}$=24.0 Hz, CO_{ax}), 205.0 (d, $^2J_{CP}$=8.8 Hz, CO_{eq}), 204.5 (d, $^2J_{CP}$=9.1 Hz, CO_{eq}), 138.0 (d, $^1J_{CP}$=24.6 Hz, *ipso*-C), 136.7 (d, $^1J_{CP}$=32.8 Hz, *ipso*-C), 136.4 (m, C7), 133.0 (d, $^2J_{CP}$=7.0 Hz, C8), 128.1-129.8 (m, C9-12 + ArC), 38.1 (dd, $^1J_{CP}$=13.5 Hz, $^2J_{CP}$=5.2 Hz, C5), 36.6 (dd, $^1J_{CP}$=14.3 Hz, $^2J_{CP}$=6.0 Hz, C2), 27.0 (dd, $^1J_{CP}$=20.0 Hz, $^2J_{CP}$=9.1 Hz, C6), 26.1 (dd, $^1J_{CP}$=15.3 Hz, $^2J_{CP}$=5.6 Hz, C3). ^{1}H NMR ($CDCl_3$): δ 6.79-7.60 (m, 14H, H9-H12 + ArH), 4.12-4.21 (m, 1H, H2), 3.85 (ddm, $^2J_{HP}$=19.9 Hz, $^3J_{HH}$=6.4 Hz, H5), 3.29 (ddm, $^2J_{HH}$=14.6 Hz, $^3J_{HH}$=1.2 Hz, 1H, H3a), 2.89 (ddm, $^2J_{HH}$=14.6 Hz, $^3J_{HH}$=7.1 Hz, 1H, H3b), 2.72-2.84 (m, 2H, H6a-b). IR (KBr): ν = 2071.0 (m), 1991.2 (m), 1930.1 (s), 1914.1 (s) (C≡O) cm^{-1}. M/*z* (%): 822 (18) [M^+], 738 (30), [M^+-3CO], 444 (50) [M^+-$Mo(CO)_{10}$], 346 (100) [M^+-$Mo_2(CO)_{10}$], 149 (100) [$C_9H_{10}P^+$].

***rac*-10b**: Mp: decomposition > 116°C. ^{31}P NMR ($CDCl_3$): δ 19.7 ($^1J_{PMo}$=26.2 Hz). ^{13}C NMR ($CDCl_3$): δ 209.8 (d, $^2J_{CP}$=24.8 Hz, CO_{ax}), 204.5 (m, CO_{eq}), 136.8 (d, $^1J_{CP}$=25.0 Hz, *ipso*-ArC), 135.8 (t, $^2J_{CP}$=$^3J_{CP}$=3.3 Hz, C7, C8), 129.6 (s, C10, C11),

128.5-129.2 (m, C9, C12, *o*+*m*+*p*-ArC), 37.5 (m, C2, C5), 27.4 (m, C3, C6). ^{13}C NMR ($CDCl_3$): δ 209.8 (d, $^2J_{CP}$=24.8 Hz, CO_{ax}), 204.5 (m, CO_{eq}), 136.8 (d, $^1J_{CP}$=25.0 Hz, *ipso*-ArC), 135.8 (t, $^2J_{CP}$=$^3J_{CP}$=3.3 Hz, C7, C8), 129.6 (s, C10, C11), 128.5-129.2 (m, C9, C12, *o*+*m*+*p*-ArC), 37.5 (m, C2, C5), 27.4 (m, C3, C6). ^{1}H NMR ($CDCl_3$): δ 7.45-7.57 (m, 4H, H9-H12), 7.20-7.27 (m, 6H, *m*+*p* ArH), 6.95-7.00 (m, 4H, *o*-ArH), 4.14 (ddd, $^2J_{HP}$=22.3 Hz, $^3J_{HH}$=5.2 Hz, $^3J_{HH}$=2.3 Hz, 2H, H2, H5), 3.11 (ddd, $^2J_{HH}$=14.5 Hz, $^3J_{HP}$=3.3 Hz, $^3J_{HH}$=2.3 Hz, 2H, H3a, H6a), 2.53 (ddd, $^2J_{HP}$=21.8 Hz, $^2J_{HH}$=14.5 Hz, $^3J_{HH}$=5.2 Hz, 2H, H3b, H6b). IR (KBr): ν = 2070.3 (s), 1988.6 (sh), 1939.9 (m), 1916.1 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{32}H_{20}O_{10}P_2Mo_2$, 821.8640. Found 821.8803. *M*/*z* (%): 822 (50) [M^+], 738 (72) [M^+-3CO], 682 (60) [M^+-5CO], 542 (15) [M^+-10CO], 444 (50) [M^+-Mo(CO)$_{10}$], 346 (100) [M^+-$Mo_2(CO)_{10}$].

11d: Isolated with phosphepine **1d**. Data obtained from differential spectra. ^{31}P NMR ($CDCl_3$): δ 4.3 (d, $^1J_{PH}$=348 Hz). ^{1}H NMR ($CDCl_3$): δ 7.50 (ddm, $^3J_{HP}$=28.9 Hz, $^3J_{HH}$=12.8 Hz, 1H, Ar-CH=), 7.27-7.57 (m, 9H, ArH), 6.29 (ddd, $^2J_{HP}$=25.7 Hz, $^3J_{HH(C)}$=12.8 Hz, $^3J_{HH(P)}$=11.2 Hz, 1H, =CH-P), 6.17 (ddd, $^1J_{HP}$=347.7 Hz, $^3J_{HH}$=11.2 Hz, $^4J_{HH}$=1.0 Hz, 1H, PH), 3.27 (s, 1H, CCH). IR (KBr): ν (cm^{-1}): 3301.06 (w), 2957.6 (w), 2942.6 (w), 2863.3 (w), 2063.4 (m, C≡O), 1983.5 (sh, C≡O), 1937.4 (s, C≡O), 1260.5 (w), 1093.9 (br, m), 1022.3 (br, m), 799.6 (m), 762.3 (w), 627.0 (s), 650.9 (s, CCH).

Evidence for disproportionation of 3a: A mixture of **3a** (10.5 mg, 0.024 mmol) and **3h** (10.9 mg, 0.025 mmol) was dissolved in THF (0.5 ml). The resulting solution was monitored by ^{31}P NMR. Alongside the signals attributed to **3a** (-89.4 ppm, s) and **3h** (-90.6, q, $^1J_{PD}$ = 53.7 Hz) the signal of PhPHD-W(CO)$_5$ grew in: -90.0 (t, $^1J_{PD}$ = 53.7 Hz). After 2hrs an equilibrium is reached, with the following intensities: PH_2:PHD:PD_2 = 1.0:0.4:0.7.

General procedure for phosphinidene reactions: The benzophosphepine complex and substrate were dissolved in dry toluene (20 mL/mmol) and placed in an oil bath at the reaction temperature until completion. The solvent was evaporated, followed by sublimation of naphthalene at 60°C/1-2 mm Hg. The residu was purified by column chromatography (1st pentane, then pentane:Et_2O=1:4) when necessary and/or crystallization (pentane, –20°C).

15d:[18] 1.5 eq. of tolan, 11h at 85°C. Yellow crystals, 75%. ^{31}P NMR ($CDCl_3$): δ -109.2. ^{13}C NMR ($CDCl_3$): δ 220.3 (d, $^2J_{CP}$=5.8 Hz, CO_{ax}), 216.3 (d, $^2J_{CP}$=16.4 Hz, CO_{eq}), 138.7 (d, $^1J_{CP}$=1.9 Hz, *ipso*-ArP), 130.9 (d, $^2J_{CP}$=14.4 Hz, *o*-ArP), 130.6 (s, *p*-ArC), 130.4 (d, $^3J_{CP}$=5.0 Hz, *o*-ArC), 130.3 (d, $^4J_{CP}$=2.3 Hz, *p*-ArP), 129.3 (d, $^1J_{CP}$=12.4 Hz, C=), 129.3 (d, $^4J_{CP}$=0.7 Hz, *m*-ArC), 128.6 (d, $^3J_{CP}$=9.7 Hz, *m*-ArP), 127.4 (d, $^2J_{CP}$=6.9 Hz, *ipso*-ArC). ^{1}H NMR ($CDCl_3$): δ 7.88-7.92 (m, 4H, ArH), 7.45-7.58 (m, 8H, ArH), 7.27-7.35 (m, 3H, ArH).

16d:[30] 2.9 eq. of *trans*-stilbene, 11h at 85°C. Light-yellow solid, ~100%. After crystallization, yellow needles, 70%. ^{31}P NMR ($CDCl_3$): δ -72.5. ^{1}H NMR ($CDCl_3$): δ 6.98-7.50 (m, 15H, ArH), 3.97 (dd, $^3J_{HH}$=10.0 Hz, $^2J_{HP}$=8.1 Hz, 1H, H(trans-Cr)), 3.55 (d, $^3J_{HH}$=10.0 Hz, 1H, H(cis-Cr)).

15e:[18] 1.1 eq of diphenylacetylene, 24h at 80°C. Small, light yellow crystals, 65%. ^{31}P NMR ($CDCl_3$): δ -167.9 ($^1J_{PW}$=261.2 Hz). ^{1}H NMR ($CDCl_3$): δ 7.85-7.89 (m, 4H, *o*-ArH), 7.50-7.57 (m, 6H, *m*+*p*-ArH), 1.70 (d, $^2J_{HP}$=5.6 Hz, 3H, CH_3P).

16e:[30] 2.9 eq. of *trans*-stilbene, 26h at 85°C. Light yellow oil, 88%. ^{31}P NMR ($CDCl_3$): δ -138.8 ($^1J_{PW}$=261 Hz). ^{1}H NMR ($CDCl_3$): δ 7.28-7.41 (m, 10H, ArH), 3.45 (d, $^3J_{HH}$=9.5 Hz, 1H, CH), 3.34 (dd, $^3J_{HH}$=9.5 Hz, $^2J_{HP}$=8.0 Hz, 1H, CH), 1.25 (d, $^2J_{HP}$=6.4 Hz, 3H, Me).

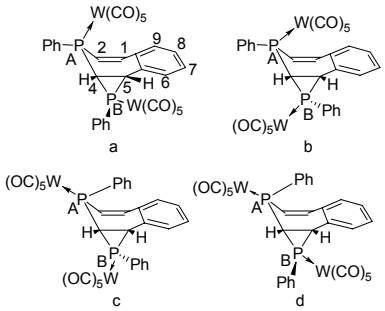
15f: 1.5 eq. of diphenylacetylene, 26h at 120°C. Orange crystals, 66%. Mp (decomp): 110°C. ^{31}P NMR ($CDCl_3$): δ -125.7 ($^1J_{PW}$=247.1 Hz). ^{13}C NMR ($CDCl_3$): δ 198.0 (d, $^2J_{CP}$=29.3 Hz, CO_{ax}), 196.5 (d, $^2J_{CP}$=7.9 Hz, CO_{eq}), 130.6 (d, $^1J_{CP}$=12.8 Hz, C=), 130.4 (s, *p*-ArC), 130.1 (d, $^3J_{CP}$=4.6 Hz, *o*-ArC), 129.3 (d, $^4J_{CP}$=0.4 Hz, *m*-ArC), 128.5 (d, $^2J_{CP}$=7.2 Hz, *ipso*-ArC), 37.7 (d, $^1J_{CP}$=2.9 Hz, CP), 28.3 (d, $^2J_{CP}$=8.9 Hz, CH_3).^{1}H NMR ($CDCl_3$): δ 7.84-7.88 (m, 4H, *o*-ArH), 7.48-7.55 (m, 6H, *m*+*p*-ArH), 1.14 (d, $^3J_{HP}$=17.4 Hz, 9H, CH_3). IR (KBr): ν = 2067.6 (w), 1980.9 (w), 1927.2 (s), 1917.4 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{23}H_{19}WPO_5$, 590.0479, Found: 590.0458. *M*/*z* (%): 590 (49) [M^+], 449 (100) [M^+-5CO-H], 393 (39) [M^+-5CO-C_4H_9].

15g:[32] 1.6 eq. of diphenylacetylene. 11h30 at 85°C. Yellow crystals. 61%. ^{31}P NMR ($CDCl_3$): δ -100.8 ($^1J_{PW}$=299.7 Hz). ^{1}H NMR ($CDCl_3$): δ 7.83 (d, $^3J_{HH}$=7.0 Hz, 4H, *o*-ArH), 7.43-7.57 (m, 6H, *m*+*p*-ArH), 2.90-3.04 (m, 4H, NCH_2), 0.98 (t, $^3J_{HH}$=7.0 Hz, 6H, CH_3).

15i: Chromatography of **15g** over SiO_2. Elution with THF. Yield depends on the time at the column. Crystallization from pentane, yellow blocks. Mp: 122-124°C. ^{31}P NMR ($CDCl_3$): δ -78.1 ($^1J_{PW}$=319.6 Hz). ^{13}C NMR ($CDCl_3$): δ 198.3 (d,

$^2J_{CP}$=38.4 Hz, CO_{ax}), 195.2 (d, $^2J_{CP}$=9.8 Hz, CO_{eq}), 147.7 (d, $^1J_{CP}$=15.0 Hz, C=), 131.1 (s, *p*-ArC), 129.9 (d, $^3J_{CP}$=5.7 Hz, *o*-ArC), 129.4 (s, *m*-ArC), 127.7 (d, $^2J_{CP}$=4.9 Hz, *ipso*-ArC). ^{1}H NMR ($CDCl_3$): δ 7.89-7.92 (m, 4H, *o*-ArH), 7.49-7.58 (m, 6H, *m*+*p*-ArH), 2.60 (s, broad, 1H, OH). IR (KBr): ν = 3524.8 (w), 3461.5 (m) (OH), 2074.5 (m), 1988.8 (m), 1933.9 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{19}H_{11}WPO_6$, 549.9803, Found: 549.98002. *M/z* (%): 550 (30) [M^+], 410 (100) [M^+-5CO], 209 (86) [PhCC(P)Ph$^+$], 178 (63) [PhCCPh$^+$].

rac-19: A mixture of **1a** (70.3 mg, 0.304 mmol) and diphenyldiacetylene (28.5 mg, 0.141 mmol) in toluene (2.9 mL) was heated at 60°C for 3 days. The solvent was evaporated, naphthalene sublimed (50°C, 1-2 mm Hg) and the crude product purified by chromatography (SiO_2, dichloromethane:pentane=1:9). The mono-adduct elutes first, followed by the main isomer. Yield: (16.1 mg, 0.015 mmol, 11%). Yellow needles. Mp: decomp. >152°C. ^{31}P NMR ($CDCl_3$): δ –137.3 ($^1J_{PW}$=274 Hz). ^{13}C NMR ($CDCl_3$): δ 197.1 (d, $^2J_{CP}$=32.5 Hz, CO_{ax}), 195.3 (pseudo-t, $^2J_{CP}$=4.0 Hz, CO_{eq}), 137.0 (m, C3,C3'), 134.0 (m, *ipso*-ArP), 132.1 (s), 131.3-131.7 (m), 129.6 (s), 129.0 (m), 126.5 (pseudo-t, $^2J_{CP}$=3.2 Hz *ipso*-ArC), 115.3 (m, C2,C2'). ^{1}H NMR ($CDCl_3$): 7.80-7.86 (m, 4H, *o*-ArH), 7.38-7.58 (m, 16H, ArH). IR (KBr): ν = 2073.3 (m), 1995.7 (m), 1986.8 (m), 1924.5 (s) (C≡O) cm^{-1}. MS: *M/z* (%): 1066 (3) [M^+], 870 (3) [M^+-7CO], 786 (5) [M^+-10CO], 352 (67) [$W(CO)_6^+$], 296 (48) [$W(CO)_4^+$], 268 (100) [$W(CO)_3^+$], 184 (20) [W^+].



21: A solution of **1a** (84.1 mg , 0.150 mmol) in toluene (1.4 mL) is heated at 60°C for 64h. After evaporation of the solvent the crude mixture is separated by column chromatography (SiO_2, 30 g, starting with 5% Et_2O in pentane, increasing to 10%). 4% of benzophosphepine **1a** is regenerated (R_f=0.37).

21a: 6.9 mg, 5%. R_f=0.24, crystals from Et_2O:pentane, -20°C. M.p. 153-158°C (decomp.).[57] ^{31}P NMR ($CDCl_3$): δ -8.4 (d, $^3J_{PP}$=14.7 Hz, $^1J_{PW}$=239 Hz,P_A), -126.9 (d, $^3J_{PP}$=14.7 Hz, $^1J_{PW}$=263 Hz, P_B). ^{13}C NMR ($CDCl_3$): δ 198.6 (d, $^2J_{CP}$=21 Hz, $CO_{ax}{}^A$), 197.4 (d, $^2J_{CP}$=34 Hz, $CO_{ax}{}^B$), 196.2 (d, $^2J_{CP}$=6.8 Hz, $CO_{eq}{}^A$), 195.3 (d, $^2J_{CP}$=7.4 Hz, $CO_{eq}{}^B$), 143.2 (pseudo-s, C1), 141-1-141.4 (m, *ipso*-Ar^A), 135.6-135.9 (m, C5a, C9a), 134.8 (pseudo-s, C9), 134.2 (d, $^3J_{CP}$=4.0 Hz, C6), 130.9-131.1 (m), 130.5 (s), 130.1 (d, $^3J_{CP}$=10.6 Hz, *m*-Ar^B), 129.2-129.4 (m), 127.6 (d, $^5J_{CP}$=2.3 Hz, C8), 124.1 (dd, $^1J_{CP}$=37.5 Hz, $^3J_{CP}$=4.7 Hz, C2), 43.0 (m, C4), 36.7 (d, $^1J_{CP}$=16.5 Hz, C5). ^{1}H NMR ($CDCl_3$): δ 7.99-8.03 (m, 2H, *o*-ArP^A), 7.64-7.68 (4H, *m*+*p*Ar^A, H6), 7.32-7.42 (m, 8H, Ar^BH, H7-H9), 7.08 (dd, $^3J_{HP}$=35.6 Hz, $^3J_{HH}$=13.7 Hz, 1H, H1), 6.35 (m, 1H, H2), 3.71-3.83 (m, 1H, H5), 3.02-3.10 (m, 1H, H4). IR (KBr): ν 2066.7 (m), 1990.5 (m), 1948.14 (s), 1929.4 (s), 1912.4 (sh) (C≡O) (cm^{-1}). HRMS: Calcd for $C_{32}H_{18}O_{10}P_2W_2$, 991.93938, Found, 991.9394. *M/z* (%): 992 (3) [M^+], 712 (12) [M^+-10CO], 558 (37) [M^+-$PhPH_2W(CO)_5$], 476 (78) [M^+-3CO-$PhPW(CO)_5$], 418 (80) [M^+-5CO-$PhPH_2W(CO)_5$], 128 (100) [$C_{10}H_8^+$].

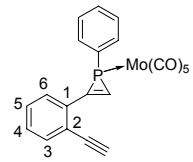
3rd frx (R_f = 0.16, 10%), 25.2 mg (17%), mixture of **21b-c**. Colorless blocks of **21b** from Et_2O:pentane = 1:4.

21b: m.p. 158-160°C (decomp.).[57]

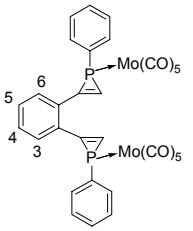
^{31}P NMR ($CDCl_3$): δ -6.6 (d, $^3J_{PP}$=11.7 Hz, $^1J_{PW}$=235 Hz, P_A), -118.8 (d, $^3J_{PP}$=11.7 Hz, $^1J_{PW}$=263 Hz, P_B). ^{13}C NMR ($CDCl_3$): δ 199.3 (d, $^2J_{CP}$=21.1 Hz, $CO_{ax}{}^A$), 197.5 (d, $^2J_{CP}$=32.6 Hz, $CO_{ax}{}^B$), 196.3 (d, $^2J_{CP}$=6.6 Hz, $CO_{eq}{}^A$), 195.3 (d, $^2J_{CP}$=7.9 Hz, $CO_{eq}{}^B$), 139.9 (pseudo-s, C1), 137.3 (d, $^1J_{CP}$=45.6 Hz, *ipso*-Ar^A), 135.0 (m, C5a, C9a), 134.4-134.5 (m, C6,C9), 131.5 (d, $^2J_{CP}$=11.0 Hz, *o*-Ar^B), 131.1 (*ipso*-Ar^B)[58], 130.8 (d, $^4J_{CP}$=2.0 Hz, *p*-Ar^B), 130.4 (d, $^4J_{CP}$=2.1 Hz, *p*-Ar^A), 129.5 (d, $^3J_{CP}$=9.2 Hz, *m*-Ar^A), 129.4 (s, C7), 128.8 (d, $^3J_{CP}$=9.9 Hz, *m*-Ar^B), 128.5 (d, $^2J_{CP}$=9.7 Hz, *o*-Ar^A), 127.4 (d, $^5J_{CP}$=2.8 Hz, C8),123.3 (dd, $^1J_{CP}$=37.5 Hz, $^3J_{CP}$=2.9 Hz, C2), 45.9 (dd, $^1J_{CP}$=27.1 Hz, $^1J_{CP}$=15.0 Hz, C4), 37.9 (d, $^1J_{CP}$=16.0 Hz, C5). ^{1}H NMR ($CDCl_3$): δ 7.79-7.85 (m, 2H, *o*-Ar^A), 7.72 (d, $^3J_{HH}$=8.0 Hz, H6), 7.64-7.69 (m, 2H, *m*-Ar^A), 7.56-7.58 (m, 1H, *p*-Ar^A), 7.35-7.38 (m, 1H, H7), 7.20-7.28 (m, 2H, 8+*p*-Ar^B), 7.00-7.02 (m, 2H, *m*-Ar^A), 6.97 (d, $^3J_{HH}$=8.0 Hz, H9), 6.51-6.55 (m, 2H, *o*-Ar^B), 5.90 (dd, $^3J_{HP}$=36.6 Hz, $^3J_{HH}$=13.9 Hz, 1H, H1), 5.60 (ddd, $^2J_{HP}$=16.5 Hz, $^3J_{HH}$=13.9 Hz, $^4J_{HH}$=2.0 Hz, 1H, H2), 3.64-3.70 (m, $^3J_{HH}$=12.9 Hz, 1H, H5), 3.19-3.22 (m, $^3J_{HH}$=12.9 Hz, $^4J_{HH}$=2.0 Hz, 1H, H4). IR (KBr): ν = 2067.9 (m), 1998.8 (w), 1979.4 (m), 1932.9 (s), 1922.8 (s), 1906.2 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{32}H_{18}O_{10}P_2W_2$, 991.93938, Found, 991.93954. *M/z* (%): (%): 992 (3) [M^+], 964 (34) [M^+-CO], 476 (96) [M^+-3CO-$PhPW(CO)_5$], 418 (100) [M^+-5CO-$PhPH_2W(CO)_5$].

21c: ^{31}P NMR ($CDCl_3$): δ –15.5 (d, $^3J_{PP}$=11.4 Hz, $^1J_{PW}$=247 Hz, P_A), -123.4 (d, $^3J_{PP}$=11.3 Hz, $^1J_{PW}$=268 Hz, P_B).

4th frx: 6.0 mg, impure **21d**. ^{31}P NMR ($CDCl_3$): δ −16.4 (d, $^3J_{PP}$=14.6 Hz, P_A), -127.9 (d, $^3J_{PP}$=14.6 Hz, P_B).



22: 2 (1.4 mmol) and **1b** (199.5 mg, 0.422 mmol) were heated in toluene (10 mL) at 75°C for 17h. The solvent was evaporated and the crude residue purified by column chromatography (SiO_2, 1% Et_2O in pentane, 20% Et_2O in pentane). Crystallization from pentane (-20°C) yielded red needles (97 mg, 0.206 mmol, 49%). Mp: 65°C. ^{31}P NMR ($CDCl_3$): δ -131.3. ^{13}C NMR ($CDCl_3$): δ 208.8 (d, $^2J_{CP}$=33.6 Hz, CO_{ax}), 205.0 (d, $^2J_{CP}$=11.2 Hz, CO_{eq}), 138.9 (d, $^1J_{CP}$=2.2 Hz, *ipso*-ArC), 135.6 (d, $^1J_{CP}$=13.6 Hz, C-C≡), 133.9 (d, $^4J_{CP}$=0.5 Hz, C3), 131.3 (d, $^3J_{CP}$=4.0 Hz, C6), 131.3 (d, $^2J_{CP}$=17.0 Hz, *o*-ArC), 130.6 (s, *p*-ArC), 130.4 (d, $^4J_{CP}$=2.5 Hz, C5), 129.3 (d, $^5J_{CP}$=0.7 Hz, C4), 128.4 (d, $^3J_{CP}$=10.2 Hz, *m*-ArC), 127.5 (d, $^2J_{CP}$=6.9 Hz, C1), 123.7 (d, $^3J_{CP}$=3.8 Hz, C2), 120.7 (d, $^1J_{CP}$=12.4 Hz, =CH), 83.9 (s, CCH), 81.5 (-CCH). ^{1}H NMR ($CDCl_3$): δ 8.56 (d, $^2J_{HP}$=22.3 Hz, 1H, =CH), 7.62-7.70 (m, 2H, H3+H6), 7.37-7.49 (m, 7H, ArH), 3.38 (s, 1H, CCH). IR (KBr): ν = 2073.5 (m), 1994.0 (m), 1920.3 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{21}H_{11}MO_5P$: 471.93982. Found: 471.94052. M/*z* (%): 472 (10) [M^+], 332 (100) [M^+-5CO], 126 (46) [$C_{10}H_6^+$].



23: To a solution of **22** (97 mg, 0.206 mmol) in toluene (4.0 mL) was added **1b** (117.0 mg, 0.248 mmol, 1.2 eq) and the resulting mixture was heated at 65°C for 24h. The solvent was evaporated and the crude product purified by chromatography (1:4 = Et_2O:pentane). The combined yield of both isomers: 86 mg, 43%. The *rac*-compound could be obtained pure after crystallization from Et_2O/pentane (yellowish plates). *rac*-**22**: 15%. Mp: decomp. > 133°C. ^{31}P NMR ($CDCl_3$): δ -135.5. ^{13}C NMR ($CDCl_3$): δ 208.3 (d, $^2J_{CP}$=34.0 Hz, CO_{ax}), 204.8 (d, $^2J_{CP}$=11.1 Hz, CO_{eq}), 137.9 (d, $^1J_{CP}$=2.6 Hz, *ipso*-ArC), 135.6 (d, $^1J_{CP}$=15.5 Hz, C-C≡), 133.3 (d, $^3J_{CP}$=5.3 Hz, C3+C6), 131.7 (s, *p*-ArC), 131.5 (d, $^2J_{CP}$=17.2 Hz, *o*-ArC), 130.8 (d, $^4J_{CP}$=2.4 Hz, C4+C5), 128.6 (d, $^3J_{CP}$=10.3 Hz, *m*-ArC), 126.8-127.0 (m, C1+C2), 121.5 (d, $^1J_{CP}$=12.1 Hz, =CH). ^{1}H NMR ($CDCl_3$): δ 8.47 (d, $^2J_{HP}$=22.0 Hz, 2H, =CH), 7.78-7.84 (m, 2H, H3+H6), 7.57-7.63 (m, 2H, H4+H5), 7.30-7.48 (m, 10H, ArH). IR (KBr): ν = 2073.4 (m), 1991.9 (m), 1925.1 (s) (C≡O) cm^{-1}. MS: 817 (<0.001) [M^+-H], 266 (100) [M^+-$Mo_2(CO)_{10}$-C_6H_6]. Elemental analysis calcd (%) for $C_{32}H_{16}Mo_2O_{10}P_2$: C 47.20, H 1.98; found: C 46.27, H 2.25.

24: 2.5 eq. of phenylacetylene, 6h at 95°C. Yellow blocks, 81%. Mp: 105°C. ^{31}P NMR ($CDCl_3$): δ -59.0. ^{13}C NMR ($CDCl_3$): δ 144.3 (s, =CPh), 142.1 (s, *ipso*-ArP), 131.1 (d, $^2J_{CP}$=14.1 Hz, *o*-ArP), 130.6 (s, *p*-ArC), 129.8 (d, $^3J_{CP}$=4.1 Hz, *o*-ArC), 129.6 (d, $^4J_{CP}$=2.5 Hz, *p*-ArP), 129.1 (s, *m*-ArC), 128.0 (d, $^3J_{CP}$=10.0 Hz, *m*-ArP), 127.5 (d, $^2J_{CP}$=6.0 Hz, *ipso*-ArC), 124.1 (s, HC=), 81.7 (s, Cp). ^{1}H NMR ($CDCl_3$): δ 8.52 (d, $^2J_{HP}$=19.3 Hz, =CH), 7.52-7.71 (m, 2H, =C(*o*-ArH)), 7.41-7.52 (m, 5H, ArH), 7.29-7.32 (m, 3H, *m*+*p*-Ar(P)H), 4.51 (d, $^2J_{HP}$=2.4 Hz, 5H, Cp). IR (KBr): ν = 1932.6 (s), 1856.2 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{21}H_{16}MnPO_2$, 386.0268, Found, 386.0247. M/*z* (%): 386 (26) [M^+], 330 (100) [M^+-2CO], 264 (32) [M^+-2CO-C_5H_6], 228 (88) [M^+-2CO-PhCCH].

25: A solution of **1c** (50.4 mg, 0.122 mmol) in 1-hexene (1.0 mL) was heated under reflux at 75°C for two days. After evaporation of the solvent the crude product is purified with chromatography (SiO_2, 1:4=toluene:pentane) yielding a yellow oil (43.8 mg, 0.119 mmol, 98%). Data in square brackets refer to the minor *anti*-isomer. ^{31}P NMR (C_6D_6): δ -77.5 [-72.7]. ^{13}C NMR (C_6D_6): δ 231.3 (broad, CO), 140.8 [136.7] (d, $^1J_{CP}$=25.4 [24.7] Hz, *ipso*-C), 131.3 [132.7] (d, $^2J_{CP}$=11.3 [10.7] Hz, *o*-ArC), 129.1 [129.4] (d, $^4J_{CP}$=2.4 [2.3], *p*-ArC), 128.5 [128.4] (d, $^3J_{CP}$=9.5 [9.4] Hz, *m*-ArC), 81.4 [81.5] (s, Cp), 32.4 [32.3] (d, $^3J_{CP}$=7.6 [4.8] Hz, CH_2CH_2CHP), 31.1 [30.9] (d, $^2J_{CP}$=1.9 [4.7] Hz, CH_2CH_3), 24.2 [23.8] (d, $^1J_{CP}$=11.7 [13.1] Hz, CHP), 22.9 [22.6] (s, CH_2CH_3), 15.5 [13.9] (d, $^1J_{CP}$=11.6 [12.0] Hz, CH_2P), 14.3 [14.0] (s, CH_3). ^{1}H NMR (C_6D_6): δ 7.28-7.35 (m, 2H, *o*-ArH), 6.91-7.03 (m, 3H, *m*+*p*-ArH), 4.16 [4.10] (d, $^2J_{HP}$=2.0 [2.1] Hz, 5H, Cp), 1.01-1.44 (m, unresolved), 0.92 [0.71] (t, $^3J_{HH}$=7.1 [7.3] Hz, 3H, CH_3), 0.64 (t, $^3J_{HH}$=7.5 Hz, 1H, HCHP). IR (KBr): ν = 1935.7 (s), 1866.3 (s) (C≡O) cm^{-1}. HRMS: Calcd for $C_{19}H_{22}MnPO_2$, 368.07379, Found, 368.07362. M/*z* (%): 368 (18) [M^+], 312 (48) [M^+-2CO], 228 (100) [M^+-2CO-C_6H_{12}].

X-Ray Crystallography

X-ray intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å) at a temperature of 150(2) K. The structures were solved with automated Patterson methods[59] (compounds *rac*-**10e**, *rac*-**19**, **21b**, *rac*-**23**, and **24**) or with Direct Methods[60] (compound *meso*-**10b**) and refined with SHELXL-97[61] on F^2

of all reflections. Geometry calculations, drawings and checking for higher symmetry were performed with the PLATON package.[62]

Crystal structure determination of *rac*-**10e**. $C_{22}H_{16}O_{10}P_2W_2$, Fw = 869.99, yellowish needle, 0.48 × 0.06 × 0.06 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 6.7509(4), b = 14.9157(8), c = 26.1982(13) Å, β = 92.038(2)°, V = 2636.3(2) Å^3, Z = 4, ρ = 2.192 g/cm^3. 49511 Reflections up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} were measured. An absorption correction based on multiple measured reflections was applied (μ = 8.89 mm^{-1}, 0.19-0.59 correction range). 6046 reflections were unique (R_{int} = 0.047). Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map and refined as rigid groups. 327 parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0176/0.0383. R1/wR2 [all refl.]: 0.0226/0.0401. S = 1.115. Residual electron density between -1.08 and 0.58 e/Å^3.

Crystal structure determination of *meso*-**10b**. $C_{32}H_{20}Mo_2O_{10}P_2$, Fw = 818.30, colorless block, 0.21 × 0.12 × 0.06 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 9.0413(1), b = 21.6707(3), c = 17.8474(3) Å, β = 111.9773(5)°, V = 3242.75(8) Å^3, Z = 4, ρ = 1.676 g/cm^3. 38814 Reflections up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.60 Å^{-1} were measured. An absorption correction based on multiple measured reflections was applied (μ = 0.93 mm^{-1}, 0.87-0.95 correction range). 5864 reflections were unique (R_{int} = 0.071). Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. H atoms at C1, C8, C9, and C10 were refined freely with isotropic displacement parameters; all other H atoms were refined as rigid groups. 439 parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0326/0.0706. R1/wR2 [all refl.]: 0.0596/0.0827. S = 1.051. Residual electron density between -0.57 and 0.69 e/Å^3.

Crystal structure determination of *rac*-**19**. $C_{38}H_{20}O_{10}P_2W_2$, Fw = 1066.18, yellow needle, 0.39 × 0.06 × 0.06 mm^3, triclinic, $P\overline{1}$ (no. 2), a = 8.0153(3), b = 10.6946(4), c = 22.3651(5) Å, α = 88.441(2), β = 83.323(2), γ = 79.194(1)°, V = 1870.34(10) Å^3, Z = 2, ρ = 1.893 g/cm^3. 44445 Reflections up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} were measured. An absorption correction based on multiple measured reflections was applied (μ = 6.29 mm^{-1}, 0.37-0.69 correction range). 8531 reflections were unique (R_{int} = 0.045). Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined as rigid groups. 469 parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0295/0.0542. R1/wR2 [all refl.]: 0.0463/0.0580. S = 1.200. Residual electron density between -0.96 and 1.10 e/Å^3.

Crystal structure determination of **21b**. $C_{32}H_{18}O_{10}P_2W_2$, Fw = 992.10, colorless block, 0.42 × 0.24 × 0.18 mm^3, triclinic, $P\overline{1}$ (no. 2), a = 10.4762(1), b = 11.3603(1), c = 14.8964(1) Å, α = 103.5604(4), β = 99.8561(5), γ = 103.9820(4)°, V = 1622.87(2) Å^3, Z = 2, ρ = 2.030 g/cm^3. 47067 Reflections up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} were measured. An absorption correction based on multiple measured reflections was applied (μ = 7.24 mm^{-1}, 0.15-0.27 correction range). 7450 reflections were unique (R_{int} = 0.029). Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. H atoms at C1, C2, C9, and C10 were refined freely with isotropic displacement parameters; all other H atoms were refined as rigid groups. 431 parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0155/0.0334. R1/wR2 [all refl.]: 0.0173/0.0339. S = 1.105. Residual electron density between -0.61 and 0.89 e/Å^3.

Crystal structure determination of *rac*-**23**. $C_{32}H_{16}Mo_2O_{10}P_2$, Fw = 814.27, yellowish plate, 0.42 × 0.33 × 0.06 mm^3, triclinic, $P\overline{1}$ (no. 2), a = 9.2748(4), b = 12.0660(6), c = 15.2717(6) Å, α = 90.529(2), β = 98.060(1), γ = 104.808(2)°, V = 1634.16(12) Å^3, Z = 2, ρ = 1.655 g/cm^3. 36889 Reflections up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} were measured. An absorption correction based on multiple measured reflections was applied (μ = 0.92 mm^{-1}, 0.50-0.95 correction range). 7481 reflections were unique (R_{int} = 0.049). Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. H atoms at C8 and C10 were refined freely with isotropic displacement parameters; all other H atoms were refined as rigid groups. 423 parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0338/0.0873. R1/wR2 [all refl.]: 0.0425/0.0935. S = 1.038. Residual electron density between -1.36 and 1.10 e/Å^3.

Crystal structure determination of **24**. $C_{21}H_{16}MnO_2P$, Fw = 386.25, yellow block, 0.36 × 0.15 × 0.12 mm^3, triclinic, $P\overline{1}$ (no. 2), a = 9.2488(1), b = 10.0296(1), c = 10.8435(2) Å, α = 110.0434(9), β = 95.2573(10), γ = 105.1996(8)°, V = 893.42(2) Å^3, Z = 2, ρ = 1.436 g/cm^3. 16043 Reflections up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1} were measured. An

absorption correction based on multiple measured reflections was applied (μ = 0.84 mm^{-1}, 0.85-0.91 correction range). 4040 reflections were unique (R_{int} = 0.047). Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Phenyl H atoms were refined as rigid groups; all other H atoms were refined freely with isotropic displacement parameters. 250 parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0289/0.0680. R1/wR2 [all refl.]: 0.0380/0.0731. S = 1.038. Residual electron density between -0.28 and 0.43 e/$Å^3$.

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Supporting Information

Supporting information containing the calculated energies and *xyz*-coordinates of the species discussed are available free of charge from the author.

7.5 Notes and References

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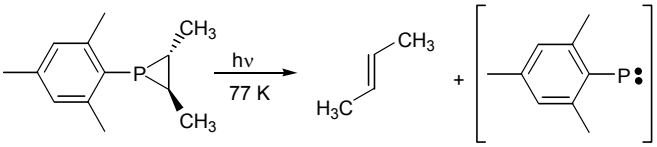
Samenvatting

Nieuwe Benaderingen voor het Toegankelijk Maken van Fosfinidenen

Het onderzoek dat in dit proefschrift is beschreven betreft een aantal manieren waarop vrije fosfinidenen en metaal-gecomplexeerde fosfinidenen toegankelijk kunnen worden gemaakt, enerzijds om de fundamentele vragen omtrent de eigenschappen van deze zeer reactieve deeltjes te beantwoorden, anderzijds om die hoge reactiviteit toe te passen in de synthese van interessante en complexe verbindingen.

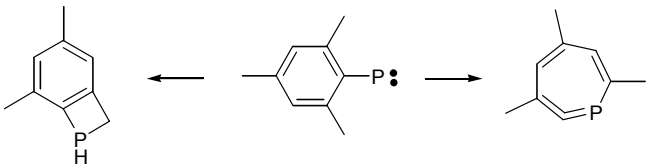
Als een fosforatoom onderdeel uitmaakt van een molecuul is het normaalgesproken verbonden aan drie andere atomen. Fosfinidenen [R-P] zijn deeltjes waarbij fosfor slechts verbonden is aan één ander atoom en deze worden daarom gekenmerkt door een hoge reactiviteit en korte levensduur. Ook met andere elementen, zoals koolstof en stikstof, zijn dit soort laag-valente verbindingen bekend, en er zijn zeer vele onderzoeken uitgevoerd waarin deze carbenen [R_2C] of nitrenen [R-N] zijn waargenomen. Echter, bij aanvang van het hier beschreven onderzoek was slechts eenmaal eerder vermelding gemaakt van experimenteel bewijs voor een fosfinideen.



1 **2**

Gaspar en medewerkers rapporteerden in 1994 dat uit fosfiraan **1**, geïsoleerd in een bevroren organisch glas, onder invloed van licht mesitylfosfinideen **2** kon worden verkregen en zij bewezen dit met behulp van elektron paramagnetische resonantie spectroscopie (EPR). Deze techniek maakt het mogelijk om paramagnetische deeltjes waar te nemen en aangezien theoretische berekeningen al hadden voorspeld dat fosfinideen **2** een triplet grondtoestand zou hebben, en daarmee paramagnetisch zou zijn, kon een signaal waargenomen worden. Afgezien van het EPR spectrum werden geen andere spectroscopische technieken toegepast. Wel werd het fosfinideen afgevangen met substraten en werd in afwezigheid daarvan een cyclopolyfosfine gevormd, wat kenmerkend is voor de reactiviteit van fosfinidenen. Andere groepen hebben deze experimenten proberen na te werken, maar slaagden daar niet in.

In **hoofdstuk 3** werd beschreven hoe wij dit experiment hebben herhaald, maar in plaats van in een organisch glas, hebben wij het fosfiraan in een edelgas matrix geïsoleerd bij de benodigde temperatuur van 15K. Na fotolyse konden wij het EPR signaal reproduceren en bovendien ook infrarood (IR) en UV/Vis spectra van fosfinideen **2** opnemen. Het UV/Vis spectrum van triplet **2** kon gereproduceerd worden met behulp van laser flash fotolyse van fosfiraan **10**, een techniek waarbij bij kamertemperatuur reactieve intermediairen snel worden gegenereerd én gemeten.



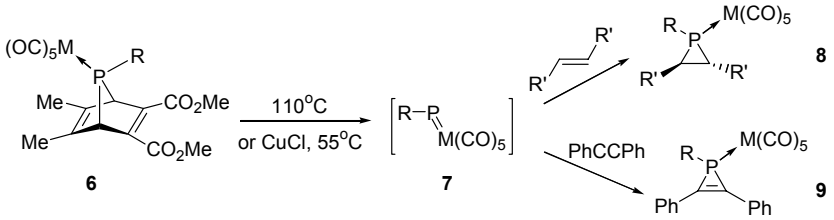
3 **2** **4**

Verder konden wij laten zien dat bij doorgaande bestraling van het fosfinideen vervolgreacties optraden. Zowel insertie in een *ortho*-methyl groep vond plaats, als insertie van het fosfor-atoom in

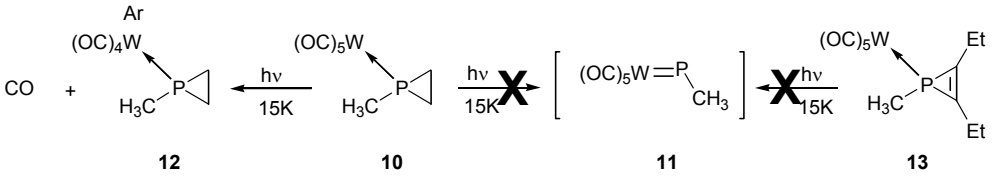
de benzeenring. Een insertie van een triplet fosfinideen in een C-H binding is niet ongewoon, maar de vorming van het cyclische fosfa-alleen **4** was onverwacht, aangezien berekeningen hadden laten zien dat het een hoog energetisch molecuul is.

In **hoofdstuk 2** werd een soortgelijke studie beschreven, maar dan met een fosfiraan gecomplexeerd aan een overgangsmetaal. Analoog aan het hierboven beschreven experiment was de verwachting dat op deze manier voor de eerste maal een neutraal electrofiel fosfinideen complex kon worden waargenomen. Op grond van de andere liganden aan het metaal kan een onderscheid worden gemaakt tussen fosfinideen complexen met een nucleofiele en complexen met een electrofiele reactiviteit. Tot nu toe zijn een aantal fosfinidenen gesynthesiseerd, die co-ordineren aan overgangsmetalen, maar opvallend is dat alle stabiele fosfinideencomplexen van het nucleofiele type zijn, met als uitzondering enkele positief geladen fosfinideencomplexen, die electrofiel reageren.

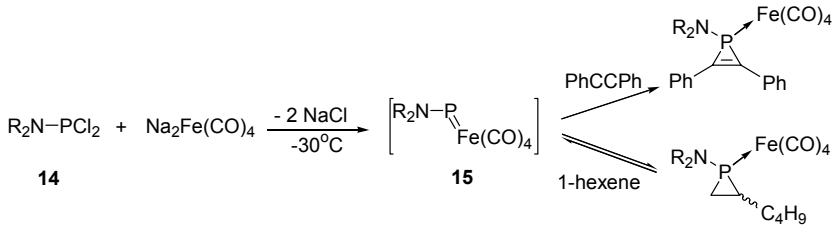
Hoewel er een zeer veelzijdige en rijke chemie ontwikkeld is op basis van de veronderstelde tussentijdse aanwezigheid van electrofiele fosfinideen complexen, zijn deze reactieve deeltjes nooit waargenomen. De meest gebruikte methode om electrofiele fosfinidenen te genereren is de verhitting van 7-fosfanorbornadieen **6** dat bij 110°C uiteen valt in een aromatische ftaaldiester en fosfinideencomplex **7**. De tussentijdse aanwezigheid van fosfinideen **7** wordt afgeleid uit de reactieproducten, waarbij de additie aan onverzadigde koolstofbindingen tot fosfiranen (**8**) en fosfirenen (**9**) kenmerkend is. De aanwezigheid van **7** volgend op de ontleding van fosfanorbornadieen **6** wordt verder ondersteund door kinetische studies, maar tot nu toe is fosfinideen **7** nog nooit direct waargenomen.



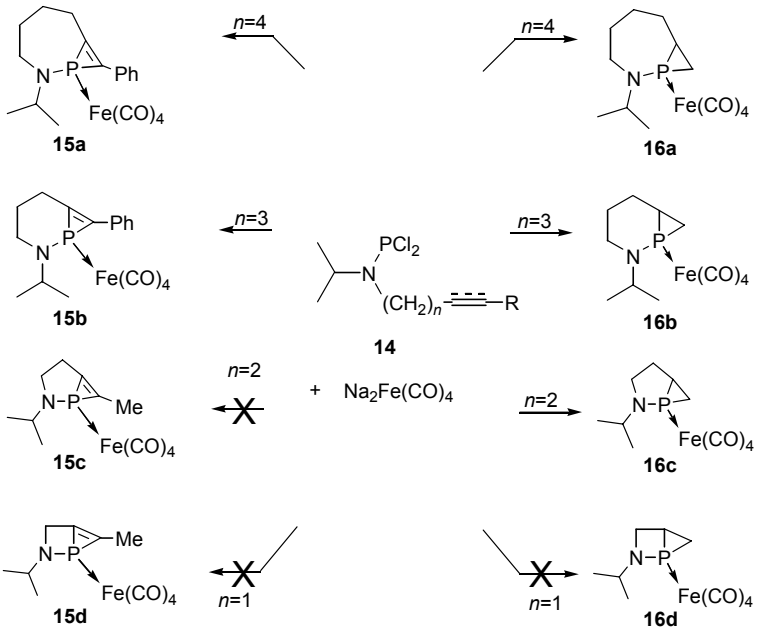
Helaas heeft de matrix isolatie studie van methylfosfiraan complex **8** ook geen bewijs opgeleverd voor de vorming van methylfosfinideen **11**. Hoewel fosfiraan **10** bij 15K onder invloed van licht reageerde, kon de vorming van een fosfinideencomplex worden uitgesloten op basis van vergelijking van de experimentele IR spectra met berekende spectra. Bovendien leidde bestraling van fosfireen **13**, dat hetzelfde fosfinideen complex zou hebben kunnen geven, tot een gelijksoortig, maar ander spectrum. Hoogstwaarschijnlijk werd één van de carbonylen van het metaal door bestraling uitgestoten, waardoor uit fosfiraan **10** $W(CO)_4$-complex **12** gevormd werd. Door de gebruikte aannames was de nauwkeurigheid van de berekende spectra niet goed genoeg om een definitief antwoord te kunnen geven. Laser flash fotolyse van **10** in cyclohexaan liet zien dat het fosfiraan loskwam van de metaal-groep en het al eerder gerapporteerde complex van $W(CO)_5$ met cyclohexaan daarbij als intermediair gevormd werd.



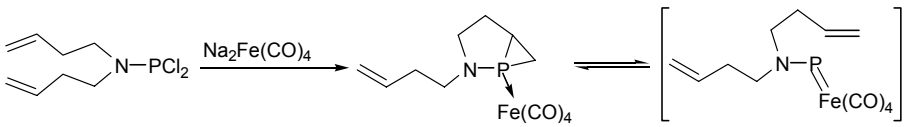
In **hoofdstuk 4** werd op een nieuwe, elegante manier bewijs geleverd voor het bestaan van electrofiele fosfinideen complexen. Daarbij werd gebruik gemaakt van een speciale methode om een ijzer aminofosfinideen te genereren. Lammertsma *et al.* hadden gerapporteerd dat de reactie van een aminodichloorfosfine (**14**) met het ijzer-dianion $Fe(CO)_4^{2-}$ bij -30°C een ijzer fosfinideen complex (**15**) oplevert, dat afgevangen kan worden met acetylenen. Ook addeerde het fosfinideen aan eindstandige olefines, maar de additie was in dit geval reversibel bij kamertemperatuur en het fosfinideen kon opnieuw worden afgevangen met acetylenen, omdat zo de stabielere fosfirenen ontstonden.



Door in één van de substituenten van stikstof in dichloor fosfine **14** een dubbele of driedubbele binding aan te brengen, werd het fosfinideen de mogelijkheid gegeven intramoleculair te adderen, waarbij bicyclische systemen zouden kunnen ontstaan. Wij hebben onderzocht welke bicyclische structuren op deze manier gevormd konden worden. Zoals te verwachten viel was het niet mogelijk om de zeer gespannen structuren **15c-d** en **16d** te maken, maar de bicyclische fosfiranen **16b-c** en het bicyclische fosfireen **15a** konden zuiver geïsoleerd worden. Van **15a** en **16b** kon de kristalstructuur worden bepaald en **16c** kon gezuiverd worden door middel van destillatie. Opmerkelijk genoeg was ook bij deze fosfiranen én zelfs bij het fosfireen de fosfinideen additie reversibel en werd na toevoeging aan fenylacetyleen het overeenkomstige fosfireen bij kamertemperatuur gevormd.

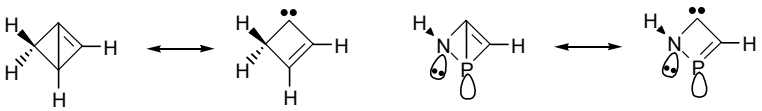


Dit dynamische gedrag werd nog diepgaander onderzocht door een dichloorfosfine met twee olefinische substituenten te laten reageren tot fosfiraan **18**. Door middel van NMR experimenten bij 74°C kon worden aangetoond dat het fosfinideen werkelijk loskwam van de ene dubbele binding en addeerde aan de andere. Dit werd zichtbaar gemaakt door de kernspin van één van de waterstoffen van het fosfiraan selectief om te draaien, waarna na 1.5 sec. ook een signaal behorend bij een olefinisch proton selectief omgedraaid bleek. Dit is alleen mogelijk als er een fysieke uitwisseling tussen de protonen plaats vindt en wordt dan ook het beste verklaard door de aanwezigheid van fosfinideen complex **19**.

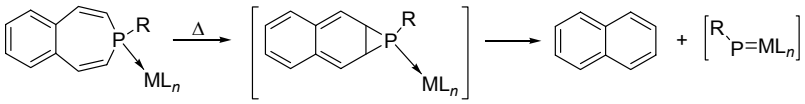


De toegankelijkheid en stabiliteit van de op deze manier gesynthetiseerde bicyclische fosfiranen en fosfirenen bleken experimenteel sterk uiteen te lopen, waarbij de ringspanning die in deze structuren verondersteld kan worden waarschijnlijk de belangrijkste bepalende factor was. Hoewel er verschillende theoretische studies zijn gedaan naar de ringspanning in cyclische systemen, is minder bekend over bicyclische structuren. Daarom is **hoofdstuk 5** gewijd aan theoretische berekeningen op een hoog niveau (G3MP2) van de ringspanning in vereenvoudigde bicyclische structuren, die corresponderen met de in het laboratorium gemaakte verbindingen. Bovendien werd de ringspanning

berekend van de afzonderlijke ringen in de bicyclische structuren en van koolwaterstof analoga. Op deze manier kon de invloed van zowel de vervanging door een heteroatoom, alsmede de fusie met een driering worden gekwantificeerd. Er kon geconcludeerd worden dat voor de bicyclische fosfiranen substitutie van koolstof met stikstof en fosfor de ringspanning verlaagt en dat dit effect voor de bicyclische fosfirenen nog groter is. Fusie met een verzadigde driering is alleen echt ongunstig voor cyclopropaan, maar fusie van cycloalkanen met een onverzadigde driering leidt tot aanzienlijk meer spanning dan in de ringen afzonderlijk, behalve bij de fusie met cycloheptaan. Bij de bicyclische fosfirenen is de spanning voornamelijk het gevolg van onnatuurlijke hoeken Door de onnatuurlijke hoeken in de kleinste systemen, vindt er een verschuiving plaats naar carbenoide structuren.



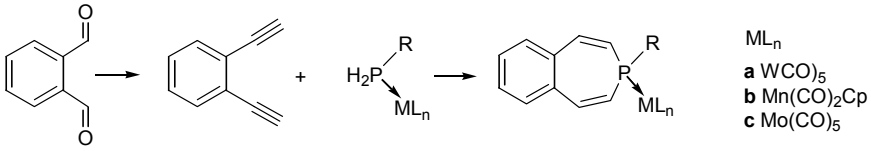
Zoals gezegd is de meest gebruikte en meest algemene methode om electrofiele fosfinideen complexen te genereren de verhitting van 7-fosfanorbornadieen complexen (**6**). Toch kleven er enkele nadelen aan deze methode, waaronder de bewerkelijkheid van de synthese, die ongeveer twee weken bedraagt. Bovendien is deze synthese door het lineaire karakter ervan niet erg flexibel voor substituent variatie. Amino-substitutie en grote substituenten zijn niet toepasbaar en alleen de groep 6 metalen kunnen worden gebruikt. In **hoofdstuk 6** werd een veelbelovende nieuwe methode om electrofiele fosfinideen-complexen te genereren geïntroduceerd, nl. benzofosfepine complexen **20**. Analoog aan de cycloheptatrieen-norcaradieen omlegging kan bij verwarming een electrocyclisatie reactie plaats vinden met een berekende barrière van 24.7 kcal/mol (R=H, M=W(CO)$_5$). Het op deze manier gevormde fosfanorcaradieen **21** kan daarop uiteenvallen in een fosfinideencomplex (**22**) en naftaleen. Dit bijproduct zou eenvoudig uit het ruwe reactiemengsel te verwijderen kunnen zijn door middel van sublimatie.



20 **21** **22**

Benzofosfepine complexen werden op convergente manier gesynthetiseerd uit fosfine complex **24** en 1,2-diethynylbenzeen, dat in twee stappen verkregen kon worden uit commercieel verkrijgbare materialen. Aangezien het fosforfragment pas in de laatste stap geïntroduceerd werd, was variatie van de gebruikte metalen eenvoudig mogelijk. De synthese en de eigenschappen van fenyl-gesubstitueerde benzofosfepine complexen van wolfraam en mangaan werden onderzocht en de kristalstructuren werden bepaald. Ook werden de reacties van **20a** met een set van standaardsubstraten uitgevoerd, waarmee werd gedemonstreerd dat benzofosfepines inderdaad als fosfinideenprecursors kunnen optreden bij relatief lage temperaturen (75-80°C). Verder werd

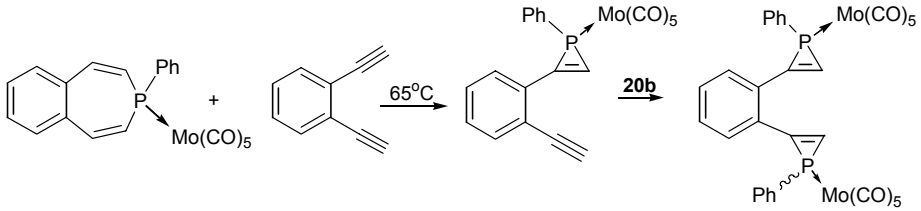
aangetoond dat de opbrengsten vergelijkbaar of beter waren dan die verkregen met de fosfanorbornadieen methode. Met name de reactiviteit van een benzofosfepine $Mo(CO)_5$ complex is zeer veel beter dan wanneer gebruik wordt gemaakt van de oude methode.



23, 91% **24** **20**

In **hoofdstuk 7** werd dieper ingegaan op deze benzofosfepine complexen. De toepassing van benzofosfepines als fosfinideenprecursors werd verder uitgebreid qua metalen (chroom) en qua substituenten, waaronder amino-substituenten en een grote substituent als de *tert*-butylgroep. De reactiviteit van deze nieuwe benzofosfepine complexen werd onderzocht en het bleek dat de temperatuur waarbij het fosfinideen vrijkomt sterk afhangt van de substituent; het metaal is daarbij minder belangrijk. Van bijna alle fosfepines werd de levensduur bepaald bij een gegeven temperatuur en één complex werd onderworpen aan een gedetailleerde kinetische analyse. Daaruit bleek dat de snelheid van ontleding slechts afhankelijk is van de concentratie van het fosfepine en onafhankelijk van willekeurig welk substraat. Dit stemde overeen met het voorgestelde fosfepine-fosfanorcaradieen mechanisme. De experimenteel bepaalde kinetische parameters kwamen bovendien goed overeen met theoretische berekeningen van deze omlegging.

In afwezigheid van substraten addeerde het fosfinideen op de C=C binding van een ander benzofosfepine molecuul en twee van de isomeren daarvan konden worden geïsoleerd en geïdentificeerd, waarbij van de meest gevormde isomeer de kristalstructuur kon worden bepaald. De additie van het fosfinideen aan diynen bleek ook mogelijk en werd toegepast in de synthese van een nieuw ligandsysteem **25**.

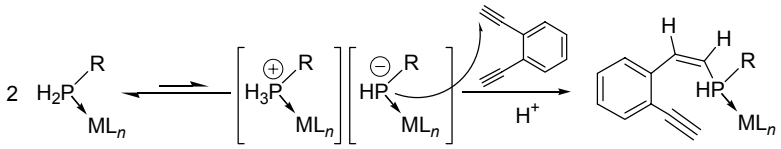


20b **23** 49% **25** - 40%

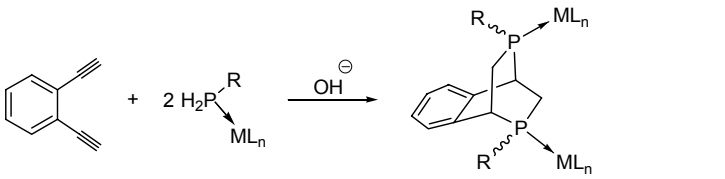
Ook werd de reactiviteit van het nieuwe mangaanfosfinideen meer in kaart gebracht en bleek het electrofiel te reageren, adderend aan 1-hexeen en fenylacetyleen. Van het zo gevormde fosfireen, het eerst bekende mangaan-fosfireen, kon de kristalstructuur worden bepaald. Een minder uitgesproken electrofiliciteit kon worden afgeleid uit het niet optreden van een additie aan digesubstitueerde olefines.

De synthese van benzofosfepines werd verder uitvoerig onderzocht. Het bleek dat voor reactie van een gecomplexeerd fosfine met 1,2-diethynylbenzeen geen base nodig was, hoewel voor een

volledige omzetting toevoeging van base gewenst was. Op deze manier konden hogere opbrengsten gehaald worden. Deze onverwacht grote reactiviteit wordt verklaard door elektronendonatie van het metaal naar het fosfine, waardoor het mogelijk is dat er een disproportioneringreactie optreedt: vorming van kleine hoeveelheden fosfonium en fosfide complex. Het fosfide-complex kan reageren met 1,2-diethynylbenzeen, waarbij na protonering een vinylfosfine (**26**) wordt gevormd. Dit intermediair was in alle syntheses goed zichtbaar in het NMR spectrum, maar kon niet zuiver worden geïsoleerd. Alle spectroscopische data wezen op een *cis*-vinylfosfine.



Indien er vanaf het begin wèl base aanwezig was, bedroeg de maximale opbrengst niet meer dan 50% en ontstonden bijproducten die in enkele gevallen geïsoleerd konden worden. Het bleek daarbij om een nieuwe klasse verbindingen te gaan, 2,5-benzeno-1,4-difosfinanen **27**, die onstonden door de reactie van twee fosfine moleculen met één molecuul diethynylbenzeen in 10-20% opbrengst. De kristalstructuur van de asymmetrische *meso* isomeer van **27a** kon worden bepaald, evenals die van de symmetrische *rac* isomeer van **27b**. De metaalfragmenten blijken *endo* georiënteerd te zijn.



Het onderzoek in hoofstuk 6 en 7 laat overtuigend zien dat benzofosfepine complexen eenvoudig toegankelijke en makkelijk te functionaliseren fosfinideenprecursors zijn, die in goede opbrengsten reageren bij lage temperaturen. Bovendien opent deze methode de deur naar nieuwe fosfinideen-complexen en anders gestabiliseerde fosfinidenen.

Afsluitend kan geconcludeerd worden dat de verschillende benaderingen om fosfinidenen toegankelijk te maken, zoals beschreven in dit proefschrift, succes hebben opgeleverd. Van een vrij fosfinideen kon het bestaan onomstotelijk worden aangetoond. De aanwezigheid van een electrofiel fosfinideencomplex kon hard worden gemaakt in een dynamisch NMR experiment en verschillende benzofosfepine complexen zijn ontwikkeld en blijken eenvoudig toegang te geven tot (nieuwe) fosfinideen complexen.

Dankwoord

één van de meest interessante gedeeltes van een cd-boekje vind ik de regels waarin de artiest alle mensen bedankt die ook maar iets met de cd te maken hebben gehad. je krijgt een indruk wie allemaal hebben meegewerkt aan zo'n project, wie de persoon hebben geïnspireerd en wie hem of haar het dichtste bij staan. ik heb altijd al een cd willen maken… het is er nog niet van gekomen. maar zo'n serie dankbetuigingen is zeker hier, aan het eind van dit proefschrift, op zijn plaats.

er wordt wel eens gezegd dat promoveren een individuele, hoogst persoonlijke prestatie is. dat is onzin.

allereerst dank aan mijn promotor, professor lammertsma, omdat u mij de gelegenheid heeft gegeven in uw groep onderzoek te doen, om in een grote vrijheid mijn dagelijkse bezigheden en de algemene lijn daarin te bepalen. op deze manier heeft u mij geholpen mij te ontwikkelen tot een kundig onderzoeker en wetenschapper.

dank ook aan mijn copromotoren dr. andreas ehlers en dr. marius schakel. dank jullie wel voor de dagelijkse begeleiding op het theoretische en praktische vlak. het was nooit moeilijk om bij jullie binnen te lopen en waardevolle adviezen te krijgen.

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ik denk aan dr. marek smoluch – voor het meten van de exacte massa's. vergeleken met de eerste twee jaar van mijn promotie was, na jouw komst naar de vu, het gemak waarmee een massa gemeten kon worden werkelijk een verademing.

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